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A Field Perspective on Groundwater Contamination

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Lecture 1

Contaminant Migration Processes Illustrated by field experiments.

A NATURAL GRADIENT EXPERIMENT ON SOLUTE TRANSPORT IN A SAND AQUIFER

I. APPROACH AND OVERVIEW OF PLUME MOVEMENT

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ABSTRACT

A large-scale field experiment on natural gradient transport of solutes in groundwater has been conducted at a site in Borden, Ontario. Well-defined initial conditions were achieved by the pulse injection of 12 m^3 of a uniform solution containing known masses of two inorganic tracers (chloride and bromide) and 5 halogenated organic chemicals (bromoform, carbon tetrachloride, tetrachloroethylene, 1,2-dichlorobenzene, and hexachloroethane). A dense, three-dimensional array of over 5000 sampling points was installed throughout the zone traversed by the solutes. Over 19,900 samples have been collected over a three-year period. The tracers followed a linear horizontal trajectory at an approximately constant velocity, both of which compare well with expectations based on water-table contours and estimates of hydraulic head gradient, porosity, and hydraulic conductivity. The vertical displacement over the duration of the experiment was small. Spreading was much more pronounced in the horizontal longitudinal than in the horizontal transverse direction; vertical spreading was very small. The organic solutes were retarded in mobility, as expected.

INTRODUCTION

The contamination of groundwater by hazardous organic chemicals has emerged in recent years to become a matter of extreme concern. Numerous instances of extensive contamination have been reported, e.g., by chlorinated solvents [Roux and Althoff, 1980]; pesticides [Guerrera, 1981]; municipal landfill leachates [Elder et al., 1981]; aromatic hydrocarbons [Yazicigil and Sendlein, 1981]; and polychlorinated biphenyls [J. R. Roberts et al., 1982]. An appreciable percentage of the groundwater used for public water supply has been found to contain detectable quantities of synthetic organic chemicals, particularly halogenated compounds containing one- or two-carbon atoms

[Westrick et al., 1984]. In industrialized urban areas, contamination by synthetic organic chemicals from multiple sources has been found to constitute a problem of regional dimensions [Fusillo et al., 1985; U.S. Environmental Protection Agency, 1985]. A salient feature of such contamination is its long-term nature: the chemicals penetrate gradually into the groundwater zone from points of surface or subsurface disposal; are transported very slowly in the direction of the hydraulic gradient; and persist in many instances for extremely long time periods.

Previous studies of groundwater contamination by synthetic organic chemicals have qualitatively documented the slow movement and persistence of the contaminants, but have generally been prevented by their retrospective nature from providing quantitative insight into processes that govern transport and fate. In most cases, it has not been feasible to quantify the initial mass of contaminant that entered the groundwater, nor in many cases to locate the emission source precisely in space and time. Furthermore, practical constraints usually have resulted in relatively sparse monitoring data which allow only approximate delineation of contaminant distribution as a function of time.

To surmount many of these limitations, we have conducted a systematic, long-term field experiment on natural gradient solute transport in a sand aquifer. The experiment was designed to produce a detailed and accurate data base describing the transport, transformation, and fate of conservative tracers and selected halogenated organic contaminants in the saturated zone. Such a data base is required for quantitative testing of the models currently hypothesized to describe the dominant fundamental processes.

In this paper we briefly review, for each process thought to influence significantly the transport and fate of dissolved contaminants, the key hypotheses that require field validation. After describing an experiment

designed to address the identified needs, we evaluate its success in creating a well-defined initial condition and in providing detailed and accurate monitoring data on solute concentration and distribution for a period of three years. In addition, an overview of the monitoring results is provided. Subsequent papers in this journal provide detailed descriptions of the methodology used to interpret the monitoring data from the perspectives of the advection and dispersion of tracers [Freyberg, 1986] and the sorption, retardation and transformation of the organic solutes [Roberts et al., 1986]. This series also includes reports on laboratory investigations of sorption and retardation [Curtis et al., 1986] and spatial variability of hydraulic conductivity [Sudicky, 1986]. The results of other related investigations have been reported elsewhere; e.g., laboratory studies of transformation of hexachloroethane [Criddle et al., 1986] and spatial variability of sorption [Mackay et al., 1986]. Additional detail on the implementation and results of the field experiment is available from the authors.

BACKGROUND

The principal processes that influence the transport behavior of an organic solute in groundwater are believed to be advection, dispersion, sorption, and transformation [Freeze and Cherry, 1979; McCarty et al., 1980; P. V. Roberts et al., 1982a; National Research Council, 1984]. Advection and dispersion describe the role of hydrodynamics in governing the rate of movement and the dilution of a solute. Sorption, or partitioning of a solute between the liquid and solid phases, results in the diminution of liquid-phase concentrations without changing the total mass of the compound, and also in the retardation of its movement relative to groundwater flow. Transformation, either by chemical reaction or microbiological interaction, results in a change in the total mass of the compound.

Advection and Dispersion

Advection refers to the mean motion of a solute pulse, whereas dispersion describes the volume-averaged deviations of concentrations from those predicted by the mean motion alone (spreading and dilution). We adopt operational definitions of advection as the vector velocity of the center of mass of a solute pulse, and of dispersion as one half the time rate of change of the spatial variance of concentration about the center of mass. Such definitions are consistent with both classic and modern theories of dispersive transport.

The classic model of hydrodynamic dispersion [cf. Bear, 1972] is developed at the scale of an REV (Representative Elementary Volume) and leads to a diffusive, or Fickian, model of transport. Interpretation of available field data suggests that dispersive spreading and dilution is non-Fickian and three-dimensionally anisotropic [Anderson, 1979; Gelhar and Axness, 1981]. Recent theoretical studies [Gelhar et al., 1979; Smith and Schwartz, 1980; Matheron and deMarsily, 1980; Dagan, 1982; Sudicky, 1983; GÜven et al., 1984], which emphasize the role of spatial variability in hydraulic conductivity and the uncertainty in our knowledge of aquifer properties, lead to models qualitatively consistent with field observations. These models indicate that there may be successive zones of transport wherein the large-scale dispersive flux is best represented by different mathematical forms, and point to asymptotically Fickian behavior under a set of assumptions that may apply to field environments. These models also demonstrate the importance of the characterization of spatial variability in aquifers and the potential utility of probabilistic predictions in dealing with spatially-variable geologic media.

Unfortunately, few data are available for meaningful testing of modern dispersion theories. In an extensive review of the available literature on field-scale transport studies, Gelhar et al. [1985] identified fifty-five

sites for which dispersivity values have been reported. Although many of these studies led to important observations on transport mechanisms, only five [Lau et al., 1957; Mercado, 1966; Molinari and Peaudecerf, 1977; Valocchi et al., 1981; and Sudicky et al., 1983] yielded dispersivity values that were evaluated as having high reliability. Of these, only one involved transport under natural gradient conditions [Sudicky et al., 1983]. None of the studies to date, however, combined the controlled initial condition, long travel distance, and detailed three-dimensional resolution of the concentration and hydraulic conductivity fields necessary for a careful evaluation of dispersive transport models.

Sorption

The concept that the transport of certain solutes in soils and aquifers is retarded by sorption is now universally accepted [Bear, 1972; Back and Cherry, 1976; Rao and Davidson, 1979; Rubin, 1983]. In laboratory studies of soils and sediments, it is generally observed that sorption of hydrophobic organic solutes in the dilute concentration range ($< 10^{-3}$M) can be approximated as reversible and described by a linear equilibrium isotherm, whose slope is termed the sorption distribution coefficient [Karickhoff, 1984]. For such solutes, the sorption distribution coefficient is thought to depend predominantly on the hydrophobicity of the solute and the organic matter (or organic carbon) content of the aquifer solids [Karickhoff et al., 1979; Schwarzenbach and Westall, 1981; Karickhoff, 1981, 1984], being relatively independent of solution composition. For transport of dilute hydrophobic solutes through homogeneous granular porous media under conditions in which sorption equilibrium is reached, the ratio of the average velocity of the water to the average velocity of the solute will theoretically be a constant, termed the retardation factor, which is linearly related to the sorption

distribution coefficient [Freeze and Cherry, 1979]. Thus, more hydrophobic solutes should be more highly retarded during groundwater transport, a trend that has been observed in previous field studies [P. V. Roberts et al., 1982b; Schwarzenbach et al., 1983].

However, there is also evidence that these relatively simple hydrophobic partitioning and retardation relationships are subject to limitations. Specific interactions between the aquifer solids and the functional groups of the solute molecule can lead to either enhancement or reduction of sorption capacity compared to expectations based on hydrophobic partitioning alone [Means et al., 1982]. In addition, sorption by mineral surfaces can approach or exceed that by the organic solid phase if the ratio of mineral surface area to organic carbon fraction is large [McCarty et al., 1980; Hassett et al., 1981; Karickhoff, 1984]. Furthermore, the assumption of sorption equilibrium may not always be justified. Some laboratory studies have indicated that desorption proceeds much more slowly than adsorption [DiToro and Horzempa, 1982]. Indeed, it has been hypothesized that sorption kinetics in real systems may be so complex that uptake and release may proceed virtually indefinitely [Karickhoff, 1984].

There is a need for field data which are sufficiently detailed to allow a thorough assessment of the applicability of sorption concepts to groundwater transport of halogenated organic compounds under natural conditions. Data are needed to determine whether retardation is constant in relatively homogeneous aquifers over large transport distances and times; whether the retardation factor observed for natural gradient transport of a given solute can be predicted from laboratory measurements of properties of the aquifer media; and whether substantial deviations from equilibrium behavior are manifested.

Transformation

Organic contaminants may potentially be transformed into other compounds by an extraordinarily complex set of chemical and biological mechanisms. The effects, relative importance, and interactions of these processes in the groundwater zone are currently not well understood.

There is good evidence that certain organic groundwater contaminants, when present at reasonably high concentrations, can be biotransformed by microorganisms attached to solid surfaces within the aquifer [Wilson and McNabb, 1983; McCarty et al., 1984]. Field studies on injection of reclaimed wastewaters into an aquifer indicate that under proper conditions trihalomethanes can be transformed with half-lives of about thirty days [P. V. Roberts et al., 1982b]. Another study on the infiltration of aromatic hydrocarbons and chlorobenzenes into groundwater from river percolation suggested that these compounds can also be transformed under proper conditions with half-lives of perhaps a few days or less [Schneider et al., 1981; Schwarzenbach et al., 1983]. These rates are too rapid to be explained by chemical transformations, and thus are probably biological in nature. Nevertheless, microbially induced changes in the groundwater environment may also enhance the opportunity for certain chemical transformations of trace organics [Castro, 1977; Bouwer et al., 1981; Giger and Schaffner, 1981].

Detailed long-term studies of the behavior of trace organic solutes under natural groundwater conditions are needed to distinguish between those compounds that can be transformed and those that persist under representative field conditions, and to confirm expectations regarding acclimation times and transformation rates based on laboratory investigations. Such field studies must yield quantitative estimates of the mass of specific organic compounds over a substantial time period to provide evidence of their disappearance or formation.

Goals of this Experiment

To meet the needs described above, we have conducted a long-term, large-scale field experiment in the saturated zone of a sandy aquifer amenable to detailed characterization. A relatively well-defined initial condition was achieved through the controlled injection into the saturated zone of a broad pulse containing known masses of inorganic tracers and halogenated organic solutes. By design, the organic solutes varied in mobility and potential for biotransformation, in order to allow assessment of the validity of the theoretical or laboratory-derived expectations. A dense, three-dimensional monitoring network, designed to yield representative groundwater samples without significantly altering the natural flow field, was sampled intensively over time. The goal of the monitoring program was to accumulate a detailed set of concentration data, corresponding to well-defined points in space and time, whose accuracy and precision could be estimated through parallel quality-assurance studies. Spatial moment analysis techniques were applied to the data to obtain quantitative estimates as a function of time of the mass of each solute in solution, the location of centers of mass of the solute pulses, and the spatial variance of the solutes' concentration distributions about the centers of mass.

These results were supplemented with field measurements of other parameters (e.g., water level as a function of space and time) and laboratory determinations of the physical, chemical, and microbiological characteristics of the aquifer within the experimental zone. The overall goals of the integrated field and laboratory efforts were:

1) To identify the physical, chemical, and microbiological processes controlling transport in the groundwater environment of the experimental site;

2) To test whether laboratory-scale understanding of the behavior of synthetic organic compounds can be used to predict field-scale transport; and

3) To assemble a data base useful for developing and validating mathematical models of groundwater transport, especially those explicitly incorporating the effects of chemical interactions, microbiological transformations, and the spatial variability of aquifer parameters.

The remainder of this paper describes the experimental site, outlines the experimental procedures and provides an overview of the results of monitoring of the solute plumes over a three-year period.

EXPERIMENTAL SITE AND AQUIFER CHARACTERISTICS

The experiment was conducted in the unconfined sand aquifer underlying an inactive sand quarry at the Canadian Forces Base, Borden, Ontario (Figure 1). The quarry is located approximately 350 m north of a municipal landfill that was in operation from 1970 to 1976. The leachate plume from this landfill has been studied extensively [Egboka et al., 1983; MacFarlane et al., 1983; Nicholson et al., 1983]. Figure 1 also indicates the sites of two previous, smaller-scale natural gradient experiments conducted by Sudicky et al. [1983] and Sutton and Barker [1985]. Figure 2 shows a schematic vertical section of the aquifer at the site. The aquifer extends about 9 m beneath the nearly horizontal quarry floor and is underlain by a thick, silty clay deposit. In the quarry area, the landfill leachate plume is confined to the bottom 2-3 m of the aquifer. As shown in Figure 2, the experiment is being carried out in the upper, uncontaminated portion of the aquifer.

The physiography, climate, and general hydrogeology of the site area have been described by MacFarlane et al. [1983]. The aquifer is composed of clean,

well-sorted, fine- to medium-grained sand. Although the aquifer is quite homogeneous relative to many aquifers of similar origin, undisturbed cores reveal distinct bedding features of potential importance to transport processes. The bedding is primarily horizontal and parallel, although some cross-bedding and convolute bedding are observed. Periodic structures are visible in some cores. The texture of individual beds and laminae ranges from silt to coarse sand with occasional pebbles.

The median grain sizes for a set of 846 samples taken from 11 undisturbed cores at Site 2 [O'Hannesin, 1981] range from 0.070 to 0.69 mm. Clay size fractions are very low, with 739 of the the samples having no measureable clay fraction, and only 8 samples showing clay fractions greater than 15% by weight. Grain roundness ranges from subangular to well-rounded.

The mineralogy of the bulk sample of aquifer material is summarized in Table 1. Quartz and feldspars predominate, with a substantial admixture of carbonates and amphiboles. Chlorite is the only clay mineral detected. The data in Table 1 are in reasonable agreement with mineralogical analyses reported elsewhere on other, smaller samples of the aquifer material [Dance, 1980; O'Hannesin, 1981].

The magnitude and variability of the porosity, bulk density, and solid density of the aquifer solids in the experimental zone were determined as follows. Four core samples (approximately 1 to 1.5 m long, 5 cm in diameter) were taken from several different locations at the site. The cores were subdivided into short vertical subsections (generally 15 cm long) and the bulk density estimated from the calculated volume and the mass measured after drying at 105°C. The volume-weighted arithmetic mean of the 36 available samples is 1.81 g/cm^3; the standard deviation of the spatial distribution of the measured values is 0.045 g/cm^3. This variability is small, but is significantly

larger than the measurement standard error, which is estimated to be 0.013 g/cm^3. The solid density of subsamples of the aquifer solids was measured by water displacement (which had been corroborated in preliminary analyses by helium pycnometry). No significant spatial variability could be detected over 26 samples. The measured value is 2.71 g/cm^3 with a measurement standard error of 0.01 g/cm^3. This estimate of solid density is consistent with the determined mineral composition of the aquifer solids [Table 1; Dance, 1980]. From the values of bulk density and solid density, the porosity of the samples was calculated. The volume-weighted arithmetic mean of the 36 samples is 0.33; the standard deviation of the spatial distribution is 0.017, which is significantly larger than the estimated measurement standard error of 0.006. However, relative to hydraulic conductivity (discussed below), the spatial variability of porosity is very small (coefficient of variation = 0.05).

The organic carbon content, specific surface area, and cation-exchange capacity of the aquifer solids are low. Preliminary analyses of the bulk sample and a number of samples taken from undisturbed cores indicate that the organic carbon averages 0.02%, ranging in individual strata from 0.01% to 0.09%, and the specific surface area averages 0.8 m^2/g, ranging from 0.6 to 1.6 m^2/g. Dance [1980] found cation-exchange capacity to vary only slightly (0.52 ± 0.09 meq/100 g) in 15 samples of the Borden sands.

Table 2 summarizes the chemical composition of the uncontaminated groundwater in the vicinity of the landfill as described by Nicholson et al. [1983], supplemented by more recent monitoring of the background water composition in the immediate vicinity of the experiment. The presence of calcium carbonate in the aquifer solids results in the high calcium content and alkalinity of the groundwater. The total dissolved solids (TDS) content is relatively low, although the water would be considered moderately hard based on the calcium

and magnesium contents. The dissolved organic carbon content (DOC) of the groundwater in the experimental zone is relatively low (< 1 mg/l), similar to high-quality surface waters. Initial dissolved oxygen measurements indicated that the aquifer was aerobic in the experimental zone (DO between 3.5 and 8.0 mg/l), but subsequent measurements showed that DO was quite variable over the field of study. The temperature of the groundwater in the vicinity of the experimental zone ranges from 6 to 15°C depending on the season. At any point in time, however, the variation of groundwater temperature with depth within the experimental zone is typically less than 2°C.

The groundwater flow system in the shallow, unconfined aquifer at Borden has been described by MacFarlane et al. [1983]. At the experimental site, the average water-table depth is about 1.0 m below the quarry floor (Figure 2). Seasonal water-table fluctuation is approximately 1.0 m over the year. Regionally, mean water-table elevations are greatest from late March to June in response to snowmelt and spring rains. Elevations then gradually decline over the summer and early fall, with recovery beginning with the autumn rains. Locally, the water table is also known to respond rapidly to intense rainfall, with saturation of the ground surface sometimes occurring for short periods of time.

The phreatic surface generally slopes in a northeasterly direction in the vicinity of the experimental site with some slight seasonal oscillation in direction in response to mounding beneath the landfill [MacFarlane et al., 1983]. This oscillation is evident in Figure 3, which presents four water-table maps for the sand quarry area. The maps were prepared using water-level measurements taken, in 1979, in a network of bundle piezometers and water-table standpipes installed throughout the area invaded by the landfill leachate plume. MacFarlane and coworkers [1983] conducted 11 monitoring episodes

throughout the year; the four depicted in Figure 3 are representative of the annual fluctuation. For convenience of comparison, only one flowline is drawn in each frame through the center of a rectangle enclosing the experimental site (the rectangle is identical to the frame of Figure 5(a)). The flow lines range in direction from about N40°E to N53°E over the course of the year.

The horizontal hydraulic gradient in the vicinity of the experimental site was observed to range from 0.0035 to 0.0054 in the 11 monitoring episodes conducted by MacFarlane et al. [1983]; the best estimate of a yearly average horizontal gradient is 0.0043 [Sudicky, 1986]. Equipotential surfaces are so nearly vertical that it is difficult to detect any vertical gradients in multilevel piezometers.

The hydraulic conductivity distribution in the aquifer at the experimental site has been studied using several techniques. Conventional slug tests [Hvorslev, 1951] were conducted in two sets of six radially arranged piezometers located at positions denoted UW-1 and UW-2 on Figure 5(a). The piezometers were constructed of 5-cm ID PVC pipe and 0.3-m long screens, finished at depths ranging from 2 m to 4.5 m below ground surface. A total of 26 slug tests were interpreted using the method described by Hvorslev [1951]. The resulting estimates of hydraulic conductivity varied from 5×10^{-5} m/s to 1×10^{-4} m/s, with a mean value of approximately 7×10^{-5} m/s.

Two long core samples of the aquifer material were also taken at the positions of the slug tests. Falling-head permeameter tests were conducted on repacked subsamples taken from contiguous 5-cm vertical intervals of these cores. The methods used for core acquisition and permeameter tests were similar to those described by Sudicky [1986]. The resulting profiles of hydraulic conductivity (measured at 22°C) are shown in Figure 4. These profiles indicate approximately an order of magnitude variaton in conductivity with depth,

a consequence of the horizontal layering of the media. In each core, the distribution of conductivity is more closely described by a lognormal distribution than by a normal distribution. The geometric means of the conductivity are approximately 10^{-4} m/s for Core UW-1 and 8×10^{-5} m/s for Core UW-2.

O'Hannesin [1981] carried out extensive grain-size distribution analyses for a set of 846 samples from 11 undisturbed cores acquired at Site 2 (see Figure 1 and discussion above). Although hydraulic conductivity measurements were not made, characteristics of the conductivity distributions were inferred using correlations between hydraulic conductivity of granular material and properties of the grain-size distribution [e.g. Masch and Denny, 1966]. O'Hannesin found that estimated hydraulic conductivity varied over a range of about one order of magnitude. While the distribution of conductivities appeared to be lognormal for some cores, lognormality could not be accepted for all cores. Further analysis of O'Hannesin's data yields estimates of mean hydraulic conductivity (corresponding to 15.6°C) varying from 7×10^{-5} m/s to 2.2×10^{-4} m/s among the cores. The standard deviation of the natural logarithm of conductivity is positively correlated with mean conductivity, ranging from about 0.25 to 1.0 for the different cores.

Sudicky [1986] presents the results of a detailed characterization of the spatial variability of hydraulic conductivity at the site based on falling-head permeameter tests of 1279 repacked subsamples taken from 32 2-m long cores. The cores were taken along two intersecting orthogonal lines approximately parallel and perpendicular to the direction of the mean hydraulic gradient, and adjacent to the zone of solute movement. The intersection of the lines of cores is denoted as UW-3 in Figure 5a. Analysis of the measured hydraulic conductivity data revealed a predominantly horizontal, lenticular structure, consistent with visual inspection and the earlier studies mentioned

above. The overall geometric mean of the [illegible] (determined at 22°C) is 9.75×10^{-5} m/s, while the standard deviation of the natural logarithm of conductivity is estimated as 0.62. Lognormality cannot be rejected as the distribution of the conductivity values. An exponential spatial correlation function is proposed to describe the covariance structure of the conductivity field. An isotropic correlation length of ~~2.6~~ 2.8 m reasonably describes the horizontal structure, while a correlation length of 0.1 m is estimated for the vertical. These correlation lengths and the vertical anisotropy are consistent with the horizontal, lenticular structure observed in the cores. 2.8

EXPERIMENTAL PROCEDURES

Injection of the Solute Pulse

An injection system was designed to approach the ideal goal of creating, essentially instantaneously and with minimal disturbance of the natural flow field, a region of well-defined geometry within the saturated zone within which selected solutes (Table 3) were distributed reasonably uniformly. Nine injection wells, arrayed as indicated in Figure 5, were each slotted and screened within the saturated zone over the vertical interval 2.0 to 3.6 m below ground surface. The injection system was designed to provide to each of the injection wells an equal and uniform flow of a solution of uniform composition.

The composition of the injection solution is listed in Table 3. Two inorganic solutes, chloride and bromide, were included as conservative tracers [Davis et al., 1980]. Five halogenated organic solutes were chosen, because they were of known or potential environmental significance and represented a range of expected mobilities and potentials for biotransformation. In Table 3, the organic solutes are listed in increasing order of hydrophobicity (as

measured by their octanol-water partition coefficient) and thus in decreasing order of expected mobility. The relative potentials for biotransformation listed in Table 3 were inferred from prior laboratory studies at Stanford University under aerobic and anoxic (methanogenic) conditions [e.g., Bouwer et al., 1981; Bouwer and McCarty, 1982, 1983].

On August 23, 1982, approximately 12 m^3 of solution was injected over a 14.75-hour period. The solution was quite uniform throughout injection, with an average composition as noted in Table 3. Also listed in Table 3 are the estimates of the injected mass of each solute, calculated as the product of the average solution concentration and the total volume injected. The injected volume was chosen to be large relative to the scales of heterogeneity of the aquifer, as well as to ensure that dispersion during transport for several years would not too rapidly reduce the solution concentrations to near background levels.

Monitoring and Analysis

The monitoring system consisted of a dense network of multilevel sampling devices similar in concept to, but providing finer resolution in the vertical direction than, the bundle piezometers developed in earlier studies at the Borden site [Cherry et al., 1983]. Figure 5(a) shows a plan view of the sampling network in place as of January 1986; the frame of Figure 5(a) is identical to the rectangle in Figure 3. Figure 5(b) depicts the vertical distribution of sampling points along the cross-section AA' indicated in Figure 5(a). The coordinate system is located such that the direction of the x-axis is N22°E while the z-datum is taken as 221.652 m above sea level, the elevation of the top of a nearby piezometer (T29) installed during previous work at the site. The horizontal spacing of the multilevel wells varied from 1.0 to 4.0 m, while the vertical spacing of the sampling points varied from

0.2 to 0.3 m. These intervals were chosen to be consistent with estimated correlation scales of hydraulic conductivity. Within most of the zone traversed by the organic solutes during the course of the experiment ($x \leq 35$ m), the multilevel samplers were constructed with Teflon sampling tubes to ensure that the well materials would not significantly affect the composition of the samples. The remainder of the multilevel wells were constructed with polypropylene sampling tubes.

Manifolds were utilized to simultaneously collect samples from all individual tubes on a given multilevel sampler. Groundwater samples were collected directly into 14-ml glass serum vials, contacting only Teflon, stainless steel, and glass. The manifold was designed to provide duplicate samples from one of the sampling points on each multilevel device. Exposure to the atmosphere was limited to 2-4 sec, during which the vials were disconnected from the system and sealed without headspace with Teflon-lined septa. Approximately 70 ml of groundwater was extracted per sample collected for organics analysis, which ensured that the well tube and sampling system were thoroughly flushed and the collected sample representative of the groundwater surrounding the sampling point. If the total extracted volume were drawn from a spherical zone within this aquifer, the zone's radius would be on the order of 4 cm. This sample analysis suggested that the sampling points would be expected to yield samples from discrete zones. This expectation was subsequently corroborated by the field results (see below).

Samples presumed to contain organic solutes were placed in insulated coolers containing cold packs and air-freighted to Stanford University for analysis. When sampling from an area traversed only by the tracers, a simpler manifold was used to collect the samples in polyethylene bottles, which were also shipped to Stanford for analysis. Simple and efficient procedures were

used for analysis of the inorganic and organic constituents. The tracer concentrations were determined by automated ion chromatography (IC), while the organics concentrations were determined, following pentane extraction conducted in the serum bottles, by gas chromatography (GC).

OVERVIEW OF MONITORING RESULTS

Delineation of the Injected Pulse

Beginning approximately 8 hr after injection ceased, the multilevel samplers in and around the injection zone were sampled in order to delineate the initial shapes of the solute pulses. At the time of sampling, the hydraulic head distribution had completely recovered to its pre-injection condition. Figure 6 presents the observed distribution of the principal tracer, chloride. In an attempt to give a three-dimensional perspective, the vertical distribution of relative concentration for each multilevel sampler is depicted at its appropriate horizontal (x,y) location. Concentrations are scaled by the average measured concentration in the injection solution as given in Table 3 (892 mg/l). For convenience in viewing, point observations are connected by straight line segments. The distribution of scaled bromide concentrations cannot be distinguished from that for chloride shown in Figure 6.

Of note in Figure 6 is the distinct variability in chloride concentration over relatively short distances, particularly in the vertical direction. In a number of cases, relative concentration varied from nearly zero to nearly one over a vertical interval of only 20 cm. Such variability over a scale of tens of centimeters is not entirely unexpected, given the distinct small-scale bedding observed in the core samples described earlier, as well as the observed vertical variability of hydraulic conductivity reported by Sudicky [1986]. The observed vertical variability of concentrations on a scale similar to that

of hydraulic conductivity indicates that the sampling protocol was successful in yielding samples from discrete zones within the aquifer. The consistency in vertical concentration distribution across sets of samplers suggests that horizontal bedding played an important role in determining the initial shape of the pulse. The row of wells at x = -1.5 m is a particularly good example of this relatively large horizontal correlation scale observed immediately after injection.

Figure 6 also reveals that only a few point observations exceeded a relative concentration of 0.9, suggesting that significant dilution occurred during the initial displacement caused by injection. However, subsequent sampling sessions have revealed that large concentrations did exist at points not sampled by the multilevel network on this first day, so that Figure 6 tends to overstate the initial dilution. Finally, Figure 6 reveals that the chloride pulse extended above the sampling network near the center of the injection zone.

In Figure 7, relative concentration profiles for carbon tetrachloride are compared within those for chloride for a representative set of multilevel samplers. In general, concentrations of the two compounds were highly correlated, such that the spatial structures of the two pulses were essentially identical. As anticipated, relative concentrations of carbon tetrachloride were usually less than those of chloride, reflecting sorption of the carbon tetrachloride on the aquifer solids. Very similar results were observed for bromoform, which is only slightly less hydrophobic than carbon tetrachloride (Table 3). Unfortunately, because of contamination of the pentane used for sample preparation prior to GC analysis, data are not available from this initial sampling session for the three more hydrophobic organics.

Monitoring of Solute Migration

The monitoring program for the experiment has focused on obtaining information at two different levels of spatial and temporal resolution. The largest fraction of our resources and efforts has been directed toward the collection and analysis of synoptic data on the solute plumes, i.e., "snapshots" of the three-dimensional spatial distribution of concentration at particular points in time. The other portion of our effort has focused on obtaining time series data of solute concentration at a relatively high sampling frequency for a few sampling points.

Table 4 summarizes pertinent information about the 20 synoptic monitoring sessions completed since the experiment began. Initially, the sampling sessions were designed to provide coverage of all of the plumes simultaneously. However, as the solute plumes separated because of differential retardation of the organics, it became more efficient to limit individual sampling sessions to either the organic solutes or the inorganic tracers.

The time series sampling program is summarized in Table 5. Twelve sample points were chosen for detailed time resolution of their concentration history. Breakthrough of all the solutes is essentially complete at the points near the injection zone, whereas breakthrough of the slower organics is not yet complete at some of the more distant points.

Altogether, more than 19,900 samples have been collected to date; approximately 90% of those samples were analyzed, the remainder having been taken outside the perimeter of the pulses. Monitoring for organics is now complete. Synoptic sampling for tracers may continue in an attempt to extend the monitored travel distance as far as possible.

In order to assess the quality and reliability of the organic solute concentration data, several studies have been conducted which have attempted

carbon tetrachloride appears to decrease somewhat with time; the plume has not traveled as far after 633 days as would have been expected on the basis of its position after 380 days, assuming its velocity were constant. The third paper of this series [Roberts et al., 1986], which examines the behavior of the organic solutes in more detail, provides clear evidence of the decreased mobility, and therefore increased retardation, of the organic solutes over time. In addition, that paper presents mass balances for the organic solutes and provides evidence of transformation of bromoform, 1,2-dichlorobenzene and hexachloroethane.

Figure 9 presents approximate concentration distributions of the chloride plume in vertical sections on or near the longitudinal axis of the plume (1 and 462 days after injection). The vertical scale of the figure is exaggerated by a factor of 3 for clarity. Because such vertical representations cannot be produced by the same procedures as the depth-averaged representations (Figure 8), the plots in Figure 9 were produced by hand-contouring of data projected onto the cross section from monitoring points whose plan positions were generally within one meter of the longitudinal axis of the plume. The contours in Figure 9 are therefore approximate representations of the vertical distributions of chloride along the centerline of the plume at the two sampling times. Two important qualitative observations can be made from an inspection of Figure 9. First, there is a small vertical component to the movement of the chloride plume. Freyberg [1986] discusses mechanisms which may account for this behavior. Second, although significant spreading in the horizontal direction is again evident, the vertical spreading is very small. This latter finding is consistent with the results of a smaller-scale tracer test in the vicinity [Sudicky, 1983] and analyses of monitoring data on the landfill chloride plume [MacFarlane et al., 1983]. Although not shown in

Overview of Plume Behavior

Figure 8 presents equal concentration contour plots of vertically averaged solute concentration for chloride ion at 1, 85, 462, and 647 days after injection and carbon tetrachloride at 16, 380, and 633 days after injection. The averaging interval is $z = -1.5$ m to $z = -7.5$ m for all chloride plots and $z = -1.5$ m to $z = -6.0$ m for carbon tetrachloride plots. The contours are obtained by bivariate linear interpolation of an estimated concentration grid, followed by Bessel function smoothing, as implemented in the SURFACE-II plotting package [Samson, 1978]. The concentration grid is constructed as an intermediate step in the moment estimation technique described by Freyberg [1986]. Although the vertical averaging, gridding, and contouring necessarily smooth the internal representation of the plume and completely obscure the vertical variability, the plots provide a good overview of the mean behavior of the solute plumes.

Initially, the plumes are nearly rectangular in plan view. The solute plumes move at an angle to the field coordinate system and, with time, become progressively more ellipsoidal. The chloride plume appears to move at an approximately constant velocity, yet a distinct bimodality develops during the first 85 days of transport and remains visible after 647 days. Significant spreading in the longitudinal direction, and its accompanying dilution, are observed for both the inorganic and organic plumes. Relatively little horizontal transverse spreading is evident.

Figure 8 shows that the mobility of the carbon tetrachloride is significantly less than that of chloride, providing qualitative evidence of retardation due to sorption. The retardation of the other organic solutes was even greater [Roberts et al., 1986], generally in accord with their hydrophobicity (Table 3). Careful inspection of Figure 8 reveals that the mobility of the

Figure 9, the vertical spreading of the organic solutes was also very small. More detailed discussion and quantitative estimates of dispersion are presented in the next paper in this series [Freyberg, 1986].

Tracer Trajectory and Velocity

Monitoring of the chloride and bromide concentrations for a three-year period allowed the estimation of the mean velocity and trajectory of the centers of mass of the migrating pulse. The methodology employed to interpret the large body of data is described by Freyberg [1986]. Both tracers were observed to travel in a nearly linear trajectory at a mean velocity of 0.091 m/day. Assuming that the chloride and bromide ions are not affected by either ion exchange or ion exclusion, which is reasonable for such a sandy aquifer, the tracer velocity may be taken as a measurement of the average linear groundwater velocity. A unique opportunity exists, therefore, for assessment of the predictive value of indirect velocity estimation methods.

Average linear groundwater velocity is most commonly estimated from measurements of the hydraulic gradient and estimates of the hydraulic conductivity and porosity of the aquifer. As discussed previously, several methods have been applied to the estimation of the hydraulic conductivity of the aquifer in the vicinity of the experimental site. The methods, whose results are listed in Table 6, include 26 slug tests conducted at Sites UW-1 and UW-2 (Figure 5), grain size analyses of subsections of 11 core samples acquired at Site 2 (Figure 1), and permeameter analyses of subsections of two cores taken at Sites UW-1 and UW-2 and of a set of 32 cores [Sudicky, 1986] taken at Site UW-3 (Figure 5). The mean estimates of hydraulic conductivity from the various methods agree quite well; the estimates differ by less than 3%, except for that derived from permeameter analyses of only two cores. Table 6 lists the average linear groundwater velocities calculated from the

mean estimates of hydraulic conductivity and the best available estimates of the mean hydraulic gradient (0.0043) and aquifer porosity (0.33). The estimated velocities range from 0.076 m/d to 0.081 m/d, approximately 10-15% lower than the observed tracer velocity (0.091 m/d). This difference may easily be accounted for by errors in the estimates of hydraulic conductivity, regional gradient, and/or porosity. For example, the negative bias in the velocity estimates would be negligible if the effective porosity with respect to flow through the aquifer [cf. Bear, 1972, p. 121] were only 10% less than the estimated total porosity.

The observed trajectory of the centers of mass of the solute plumes over the two-year monitoring period was N47.5°E [Freyberg, 1986]. The trajectories obtained from the water-table maps (Figure 3) range from about N40°E to N53°E. There is good agreement between the predicted and observed trajectories, considering that the network of water-table monitoring points used to create the water-table maps was sparse in the vicinity of the experimental site. Nevertheless, the sparse network is relatively representative of monitoring systems used in investigations of contaminant distribution at waste disposal or chemical spill sites. It appears, then, that water-table monitoring at a coarse scale in sand and gravel aquifers, coupled with careful interpretation of results, may provide a sufficiently accurate prediction of plume trajectory for many purposes. It is important to note, however, that the plumes' trajectory in our experiment differed by approximately 25° from our earliest expectations based on less thorough analysis of water level data. Thus the monitoring network was extended based on tracer observations obtained during the transport experiment itself. This flexibility in incorporating feedback from the experiment to modify the sampling grid and schedule was an integral feature of our approach, and requisite for its success.

SUMMARY AND CONCLUSIONS

A relatively large-scale, long-term controlled field experiment on solute transport in groundwater under natural gradient conditions was initiated in August, 1982. The goal of the experiment was to produce a detailed data set describing transport and fate of two inorganic tracers and five representative halogenated organic solutes which could be used to examine the validity of hypotheses concerning the effects of advection, dispersion, sorption, and transformation.

Reasonably well-defined initial conditions were achieved by injecting a large volume (12 m^3) of groundwater uniformly spiked with known masses of the solutes into an uncontaminated portion of the saturated zone of an unconfined sand aquifer. A dense, three-dimensional array of sampling devices was installed throughout and surrounding the zone traversed by the solutes as they migrated under the influence of the natural hydraulic gradient. To date over 19,900 samples have been collected, the majority taken in 20 sessions to yield "snapshots" of the solute pulses in three dimensions. Monitoring at several points within the sampling array has been conducted at a higher frequency to yield detailed concentration histories (breakthrough curves).

The monitoring session immediately following injection indicated that there was distinct variability in tracer distribution over relatively short distances, particularly in the vertical direction, apparently influenced by the horizontal bedding known to characterize the aquifer. Nevertheless, the spatial distributions of two of the organic solutes were essentially identical to that of the tracers, indicating success in creating initially congruent pulses, as desired.

We have found that spatial moment analysis techniques can successfully be applied to the snapshot data. Our quality-assurance investigations have

indicated that the experiment was successful in yielding a set of solute concentration data with good precision and reproducibility. The laboratory procedures for organics analysis were found in general to introduce a negative bias on the order of 10%. Standard errors of analyses of quality-control samples and standard deviations of replicate field-sample analyses were on the order of 20% of the expected or mean value. Thus the quality of the field data was in the range of normal expectations for careful sampling and analytical technique when dealing with volatile organic solutes.

In summary, the experiment appears to have met its primary goal. A spatially and temporally detailed, high-quality data set has been collected on the distribution of seven solutes in three dimensions as the solutes migrated under the influence of the natural hydraulic gradient for a period of over three years. Because of the resolution inherent in the data and their amenability to analysis by spatial moment techniques, the experimental data can be used for quantitative testing of hypotheses concerning advection, dispersion, sorption and transformation. In this paper, observed advective characteristics (tracer trajectory and velocity) were shown to compare favorably with predictions made by conventional techniques, i.e., water-table mapping coupled with porosity estimates and hydraulic conductivity determination by several methods. Additional and more detailed analyses and applications of the data are the topics of subsequent papers in this journal. Those papers 1) present the methodology for the moment analysis and interpret the first and second moments of the tracer data from the viewpoint of velocity and dispersion [Freyberg, 1986]; 2) explore the relationship between the aquifer's spatial structure and the observed tracer behavior [Sudicky, 1986]; 3) compare the mobility of organic solutes with that of anionic tracers, and investigate the time-dependence of retardation as well as the conservation of mass for the

organic compounds in the aquifer over the course of the experiment [Roberts et al., 1986]; and 4) evaluate the evidence supporting sorption as the primary factor causing retardation of organic solutes in this experiment [Curtis et al., 1986].

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FIGURE LEGENDS

Figure 1. Experimental site. The rectangle within the sand quarry illustrates the location of the transport experiment and matches the frame of Figure 5a. Also shown is the approximate extent of contamination from the landfill in 1979, as delineated by a 10 mg/l chloride isopleth. Rectangles 2 and 3 mark the locations of previous smaller-scale tracer tests [Sudicky et al., 1983, and Sutton and Barker, 1985, respectively].

Figure 2. Approximate vertical geometry of aquifer along section AA' (Figure 1). The rectangle illustrates the vertical zone in which the experiment was conducted, which is above the landfill leachate plume (denoted by 10 mg/l chloride isopleth from 1979 data).

Figure 3. Water-table maps for the experimental site and vicinity. The rectangles mark the site location and match the frame of Figure 5a. Maps were prepared from results of 4 monitoring episodes conducted by MacFarlane et al. [1983]. The elevations of water level contours are given in meters above sea level.

Figure 4. Hydraulic conductivity versus depth ~~for~~ at two locations. Analyses of 5-cm contiguous subsections of core samples taken at locations shown in Figure 5 were conducted with a falling-head permeameter. The missing data correspond to depth intervals for which there was no core recovery.

Figure 5. Locations of multilevel samplers and injection wells as of January 1986: a) plan view; b) approximate vertical distribution of sampling points (+) projected onto cross-section AA' (vertical exaggeration = 4.6). The positions labeled UW-1 and UW-2 in frame a are the locations of piezometer nests and core samples discussed in the

text. The position labeled UW-3 is the center of a set of 32 cores taken in two intersecting and orthogonal lines by Sudicky [1986]. The solid vertical lines in frame b indicate the location and screen length of the injection wells.

Figure 6. Relative concentration distribution of chloride on August 24, 1982, one day after injection.

Figure 7. Vertical profiles of relative concentration of chloride and carbon tetrachloride at several sampling locations.

Figure 8. Vertically averaged concentration distribution of two solutes: a) chloride ion, 1, 85, 462, and 647 days after injection (averaging interval: $z = -1.5$ m to $z = -7.5$ m) and b) carbon tetrachloride, 16, 380, and 633 days after injection (averaging interval: $z = -1.5$ m to $z = -6.0$ m).

Figure 9. Approximate concentration distributions of chloride (1 and 462 days after injection) along vertical cross section AA', the horizontal axis of the plume (vertical exaggeration = 3). The contours depicted for the 1-day and 462-day plumes are: 10, 100, 300, and 600 mg/l; and 10, 30, 100, and 300 mg/l; respectively.

TABLE 1

Mineralogy of a Bulk Sample of the Aquifer Material

Component	Percent of Total*
Quartz	58%
Feldspars	19%
Carbonates	14%
Amphiboles	7%
Chlorite	2%
	100%

*Detemined by X-ray diffraction.

TABLE 2

Background Groundwater Characteristics

Parameter	Units	Range	Source*
Ca^{2+}	mg/l	50-110	1, 2
Mg^{2+}	mg/l	2.4-6.1	1, 2
Na^{+}	mg/l	0.9-2.0	1, 2
K^{+}	mg/l	0.1-1.2	1, 2
Alkalinity (as $CaCO_3$)	mg/l	100-250	1
Cl^{-}	mg/l	1-3	1, 2
$SO_4^{=}$	mg/l	10-30	1
NO_3^{-}	mg/l	< 0.6	1
TDS	mg/l	380-500	1
DOC	mg/l	< 0.7	2
DO	mg/l	0-8.5	2
Temperature	°C	6-15	1, 2
pH	-	7.3-7.9	2

*1, Nicholson et al. [1983]. Results have been converted from mM to mg/l, except for alkalinity; 2, This work.

TABLE 3

Injected Solutes and Their Properties

Solute	Injected Concentration (mg/l)	Injected Mass (g)	Octanol-Water Partition Coefficient (K_{ow})	Potential for Biotransformation*	
				Aerobic	Anoxic†
Tracers					
Chloride Ion	892.	10,700	-	-	-
Bromide Ion	324.	3,870	-	-	-
Organic Solutes					
Bromoform	0.032	0.38	200	-	++
Carbon Tetrachloride	0.031	0.37	500	-	+
Tetrachloroethylene	0.030	0.36	400	-	+
1,2-Dichlorobenzene	0.332	4.0	2500	+	-
Hexachloroethane	0.020	0.23	4000	?	?

*-, little potential for biotransformation; +, moderate potential for biotransformation; ++, good potential for biotransformation; ?, potential for biotransformation unknown at onset of this work.

†Methanogenic conditions.

TABLE 4

Summary of Synoptic Monitoring Program

Date	Days Since Injection	Solutes		Number of Samples Analyzed
		Tracers	Organics	
08/24/82	1	X	X	392
09/01/82	9	X	X	419
09/08/82	16	X	X	408
09/21-22/82	29	X	X	629
10/05-06/82	43	X	X	671
10/25-26/82	63	X	X	700
11/16-17/82	85	X	X	712
05/09-11/83	259	X		1219
06/22/83	303		X	233
07/19-20/83	330		X	1150
07/21/83	332	X		362
09/07-08/83	380		X	839
09/08-09/83	381	X		496
10/04/83	407		X	949
10/26-28/83	429	X		1883
11/28/83	462	X		1343
05/17/84	633		X	1122
05/31-06/02/84	647	X		958
08/01-02/84	709		X	1119
06/26-28/85	1038	X		1205

TABLE 5

Summary of Time Series Monitoring Program

Sample Point (x,y,z) (m)	Duration	Number of Samples Collected as of 1/1/86
2.5, 0.0, -3.20	Aug. 82 - Dec. 83	188
2.5, 1.25, -3.62	Aug. 82 - Dec. 83	188
5.0, 0.0, -3.26	Aug. 82 - Dec. 83	183
10.0, 4.6, -3.88	Nov. 83 - Jun. 85	45
10.0, 4.6, -4.48	Nov. 83 - Jun. 85	27
13.1, 4.05, -3.42	Jul. 84 - Jun. 85	32
13.1, 4.05, -3.72	Jul. 84 - Jun. 85	31
18.0, 9.0, -4.13	Mar. 83 - Jun. 85	119
18.0, 9.0, -4.73	Mar. 83 - Jun. 85	121
21.0, 9.0, -4.17	Mar. 83 - Jun. 85	117
21.0, 9.0, -4.77	Mar. 83 - Jun. 85	117
24.0, 9.0, -4.76	Mar. 83 - Nov. 83	78

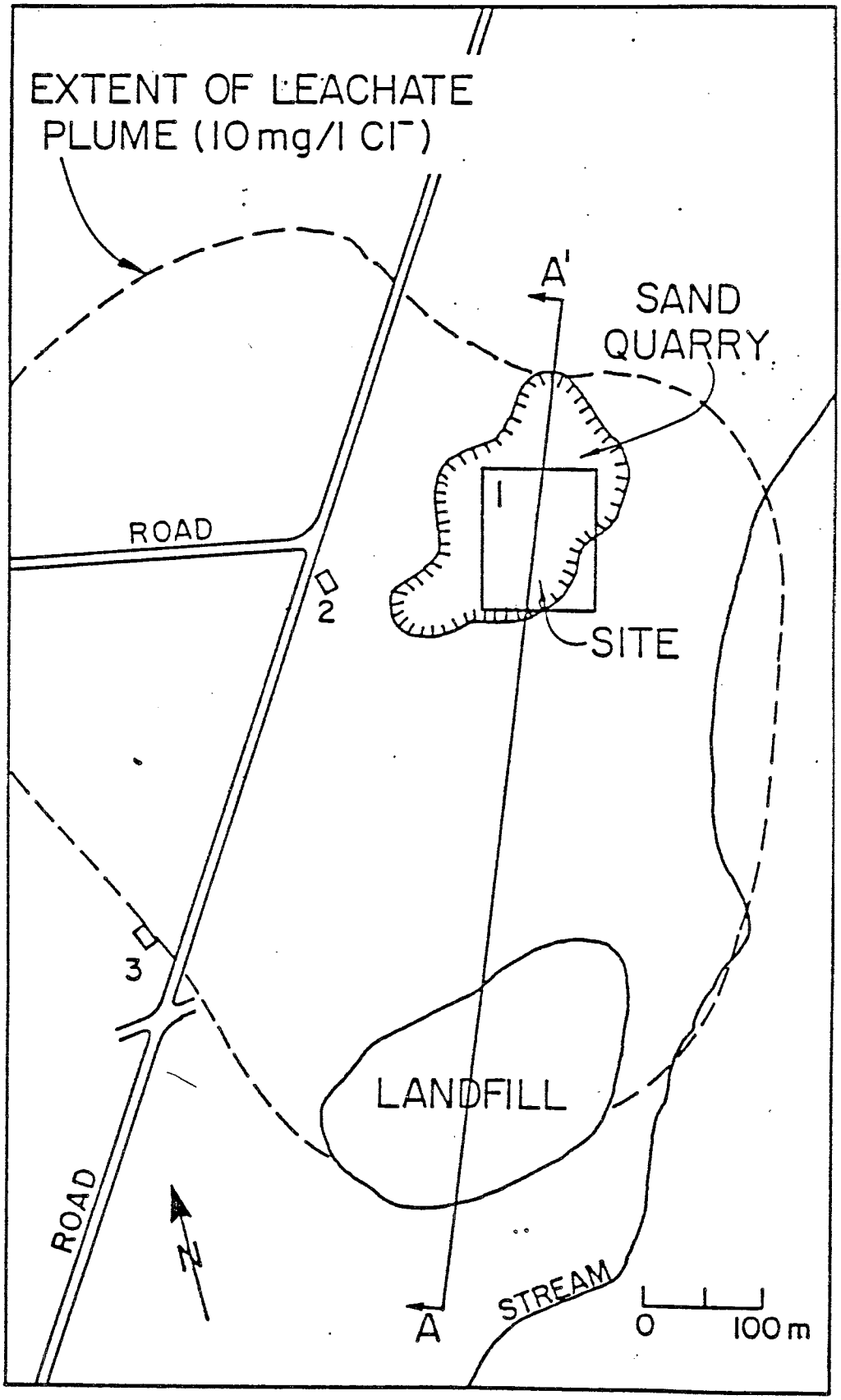
TABLE 6

Comparison of Methods for Estimating Average Linear Groundwater Velocity

Method	Estimates of Hydraulic Conductivity v 10^5 (m/s)		Estimated Average Linear Groundwater Velocity (m/d)
	Range	Mean	
Slug Tests	5 to 10	7	0.078*
Core Sample Analyses			
Grain Size Analyses† 11 cores (Site 2)	0.03 to 76	7.1	0.079*
Permeameter Analyses†			
2 cores (UW-1, UW-2)	0.1 to 15	6.7	0.076*
32 core set (UW-3)	0.04 to 15	7.2	0.081*
Natural Gradient Tracer Test	-	-	0.091

*Calculated using estimated hydraulic conductivity and assuming the mean hydraulic gradient and aquifer porosity are 0.0043 and 0.33, respectively.

†Temperature corrections have been made to adjust hydraulic conductivity values to 10°C.


EXTENT OF LEACHATE
PLUME (10 mg/l Cl⁻)
A'
SAND
QUARRY
1
ROAD
2
SITE
3
LANDFILL
ROAD
N
A
STREAM
0
100 m

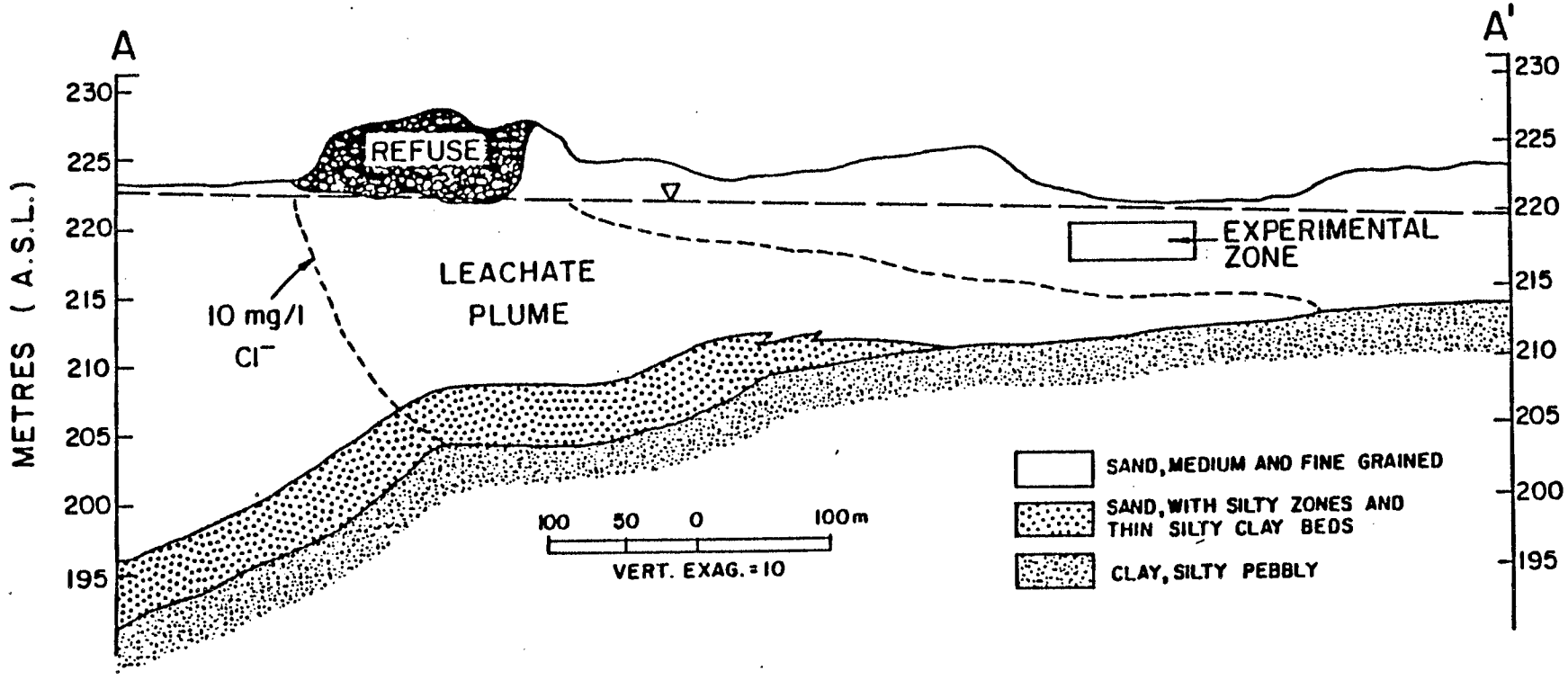

A
A'
230
225
220
215
210
205
200
195
METRES (A.S.L.)
REFUSE
LEACHATE
PLUME
10 mg/l
Cl⁻
EXPERIMENTAL
ZONE
100 50 0 100m
VERT. EXAG. = 10
SAND, MEDIUM AND FINE GRAINED
SAND, WITH SILTY ZONES AND
THIN SILTY CLAY BEDS
CLAY, SILTY PEBBLY

Fig. 2.

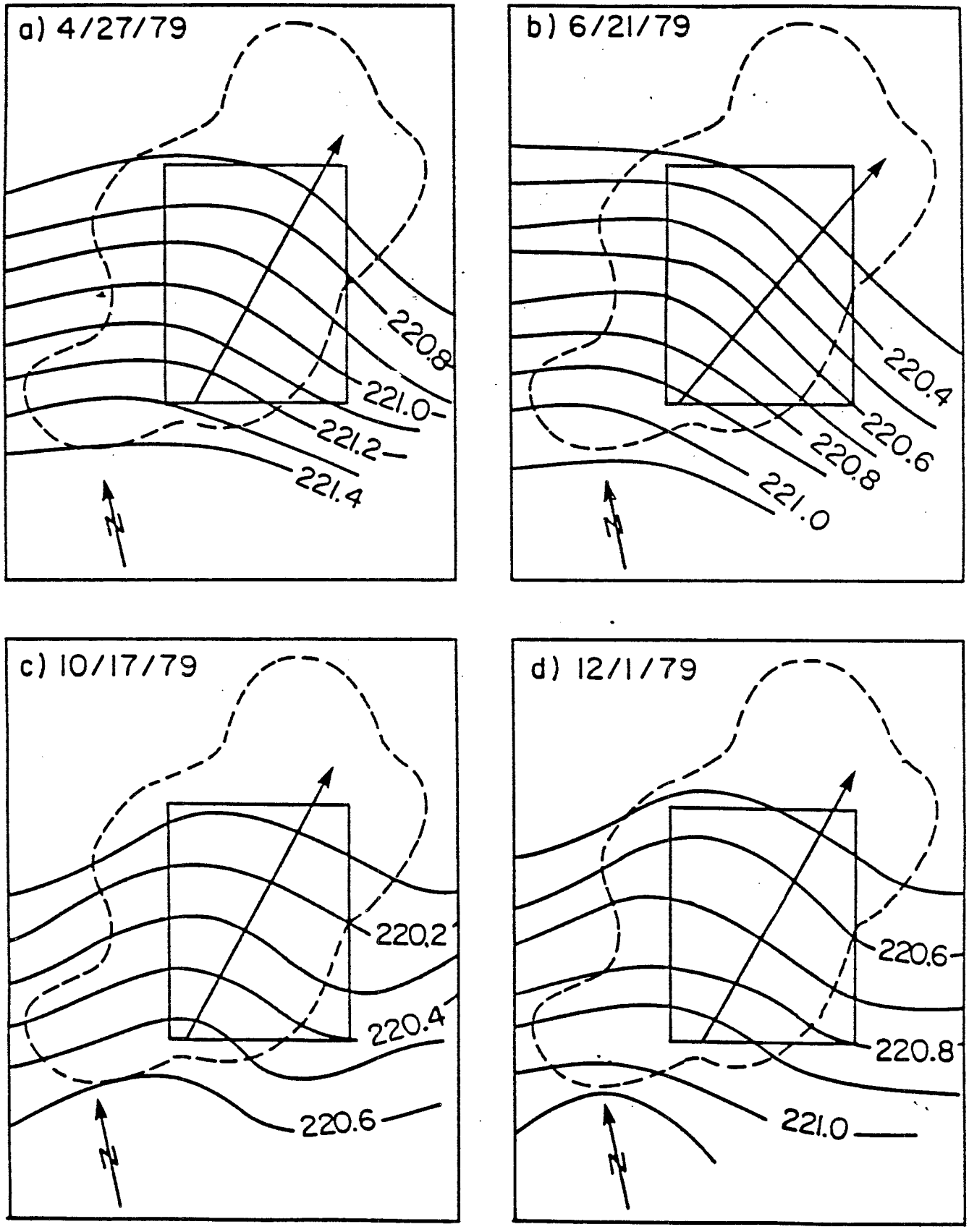
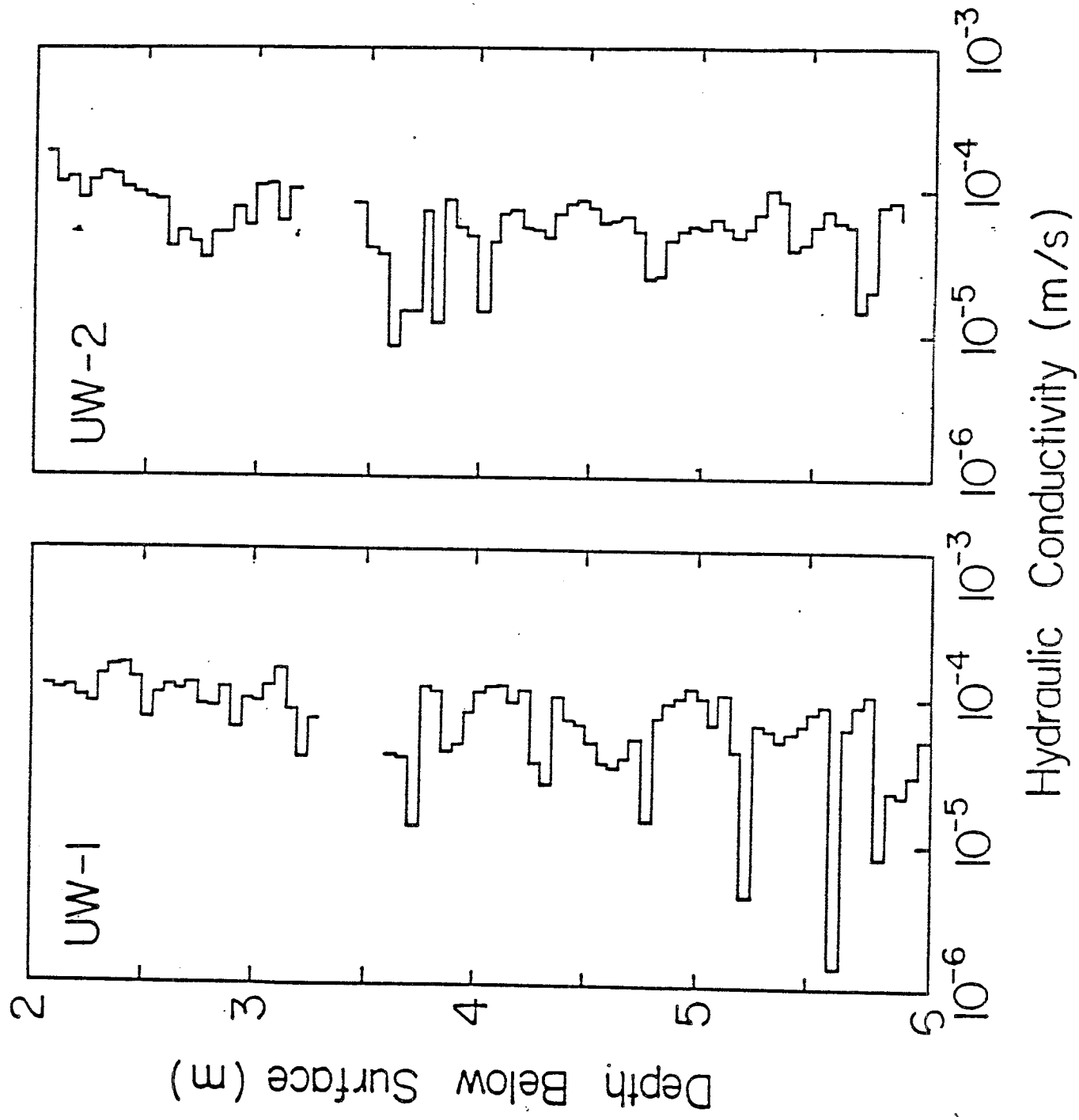

a) 4/27/79
220.8
221.0
221.2
221.4
N
b) 6/21/79
220.4
220.6
220.8
221.0
N
c) 10/17/79
220.2
220.4
220.6
N
d) 12/1/79
220.6
220.8
221.0
N

Fig. 4.


UW-2
UW-1
Depth Below Surface (m)
2
3
4
5
6
10^{-6}
10^{-5}
10^{-4}
10^{-3}
Hydraulic Conductivity (m/s)

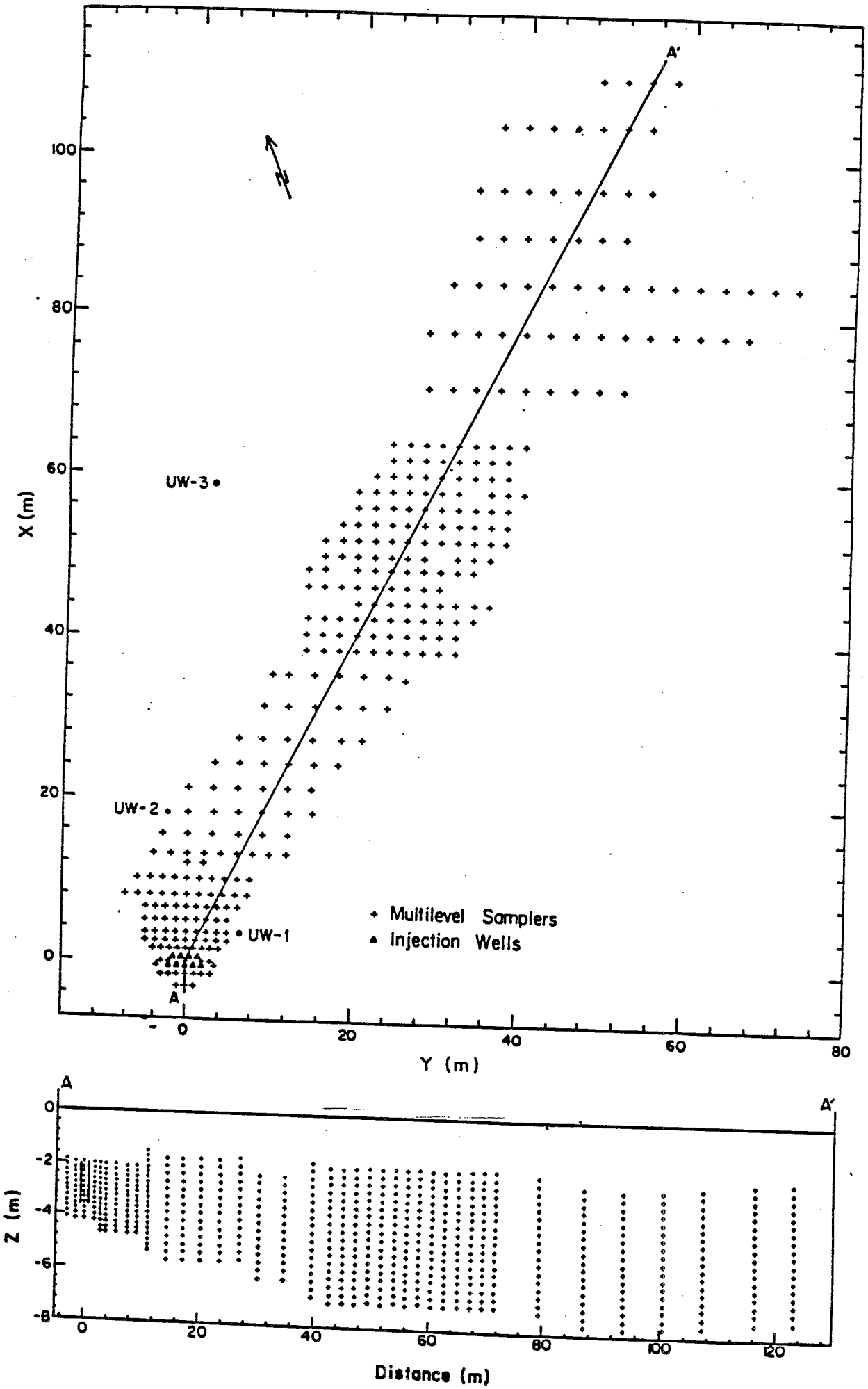
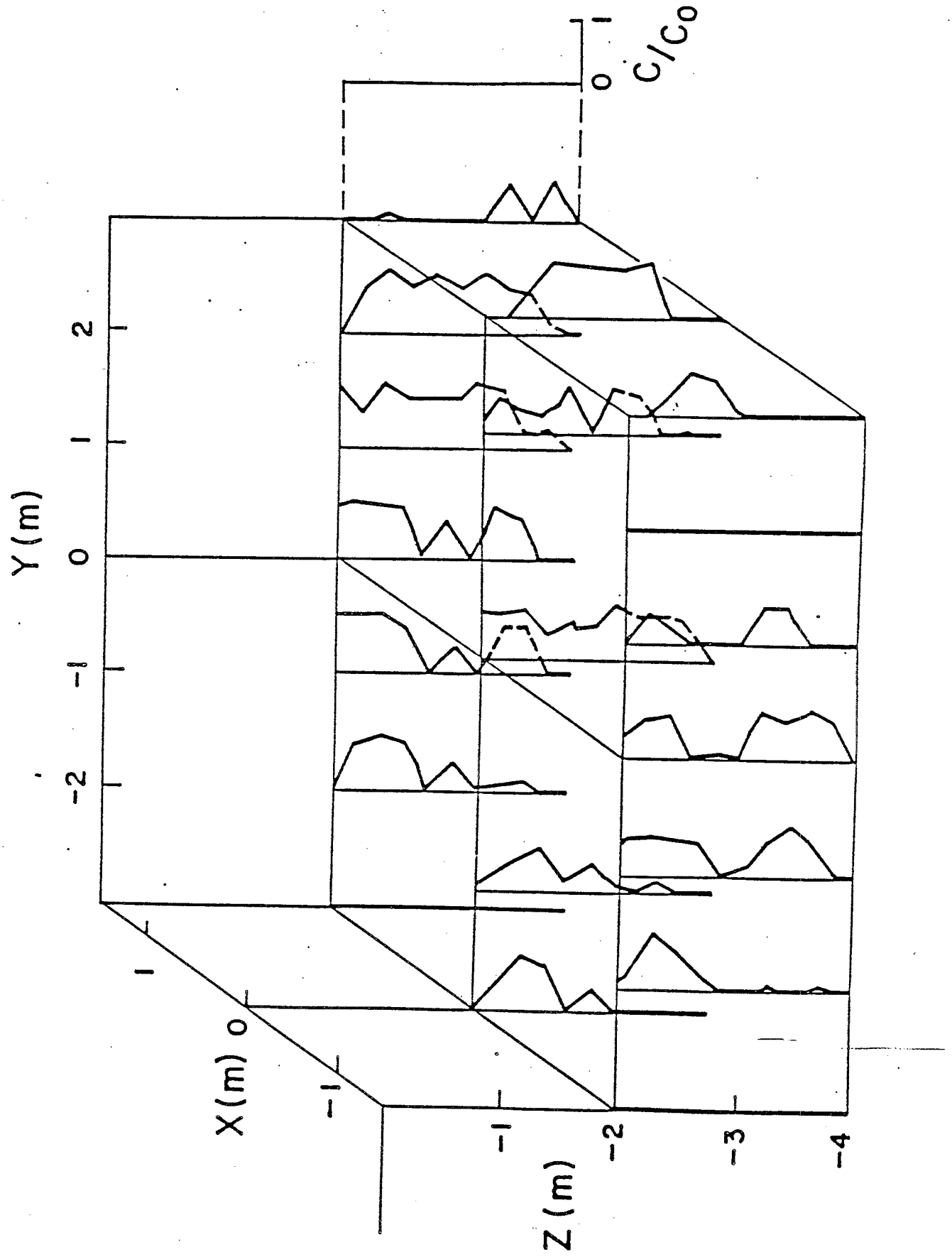

A'
100
80
60
40
20
0
X (m)
UW-3
UW-2
UW-1
A
Multilevel Samplers
Injection Wells
0
20
40
60
80
Y (m)
A
A'
0
-2
-4
-6
-8
Z (m)
0
20
40
60
80
100
120
Distance (m)

Fig. 6.



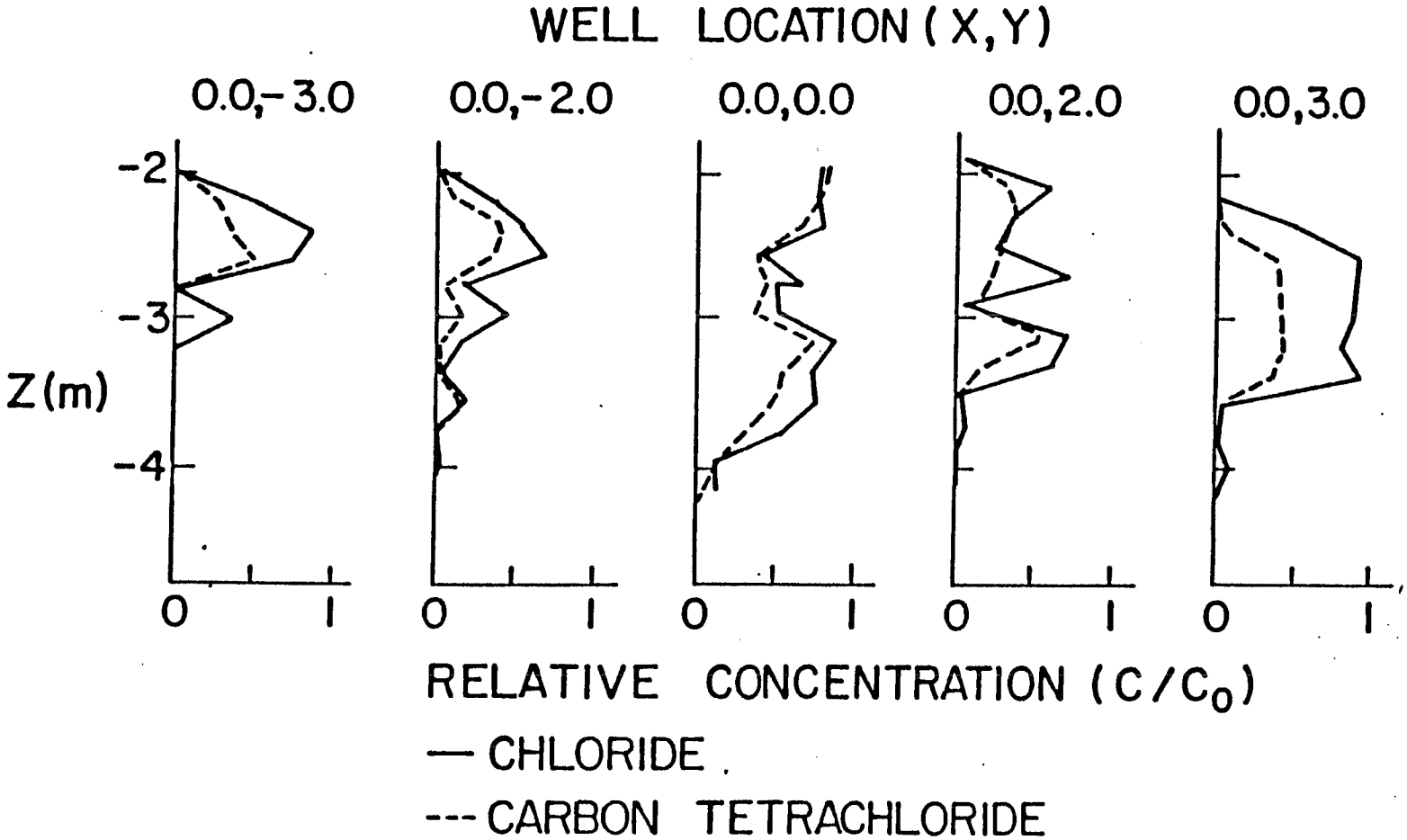
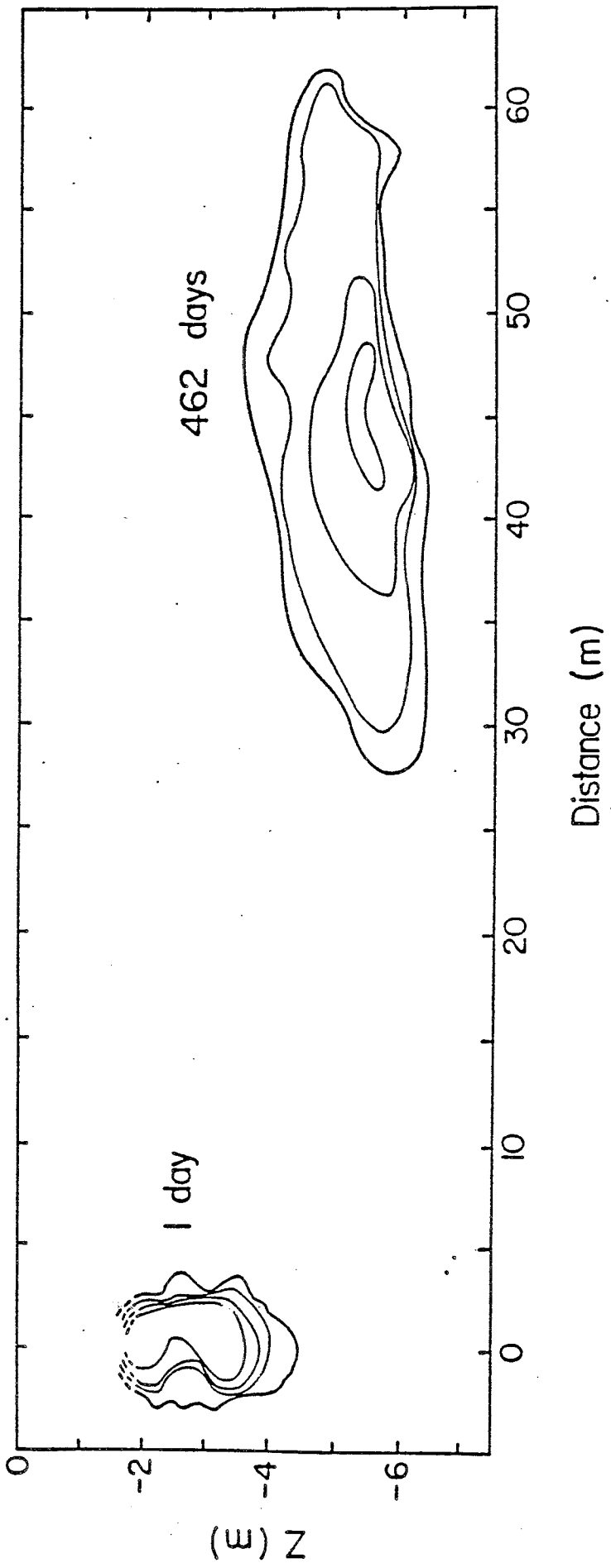

WELL LOCATION (X,Y)
0.0,-3.0
0.0,-2.0
0.0,0.0
0.0,2.0
0.0,3.0
-2
-3
-4
Z(m)
0
1
RELATIVE CONCENTRATION (C/C0)
— CHLORIDE
--- CARBON TETRACHLORIDE

Fig. 7.

Fig. 7.



A Natural-Gradient Tracer Study of Dissolved Benzene, Toluene and Xylenes in Groundwater

by

G.C. Patrick and J.F. Barker

ABSTRACT

A solution containing a known mass of dissolved mono-aromatic hydrocarbons (benzene, toluene, and xylenes) and chloride was injected as a slug into an unconfined shallow glaciofluvial sand aquifer. Transport of the constituents has been monitored using a dense array of multilevel sampling piezometers and a series of five three-dimensional 'snapshots' of the plumes have been obtained.

Vertically averaged concentrations of the chemical constituents have been used to define the horizontal aspect of the plumes and calculations of the centres of mass for each constituent have been performed. Results indicate that the hydrocarbons are all retarded relative to the chloride tracer, and that substantial mass losses of all hydrocarbon constituents have occurred. The losses, which are over 90% for all but benzene, have occurred under aerobic conditions within the aquifer and can be attributed to biodegradation. The degree of retardation is similar to that which can be predicted using octanol-water partition coefficient formulations with benzene the least, and xylenes the most retarded. The constituents are relatively mobile, however, in the low organic carbon content aquifer. Retardation factors range from only 1.2 for benzene to approximately 1.4 for xylenes.

Vertically, the plumes have assumed a distribution which reflects the heterogeneities of the aquifer material. The vertical scale of heterogeneity is of the order of 0.01 m, and hydraulic conductivity contrasts of up to an order of magnitude exist among layers. Retardation has occurred along individual layers with the result that concentration-depth profiles at individual locations appear erratic. These profiles illustrate the potential difficulties in monitoring contaminant migration in heterogeneous systems.

INTRODUCTION

Aquifer contamination by organic chemicals frequently results from the accidental spill or loss of a product to the soil. Because most organic fluids are soluble to some extent in water, a plume of dissolved constituents can form which may eventually occupy a significant volume of the aquifer. The rate at which the plume migrates and is attenuated is determined by many processes which, for organics, may include transport by the bulk movement of the groundwater, dispersion, sorption, volatilization, and chemical and biological transformations.

Our present understanding of the behaviour of many organics in groundwater is relatively vague. The natural migration of organic chemicals has been studied for the most part, at sites where the volumes and masses of the chemical constituents are not known, and where the hydrogeologic regime is not well defined. An alternative method of study is to perform a controlled injection experiment using known volumes and masses of constituents at a site where the hydrogeology is known. By monitoring the plumes, the location, size, shape, and changes in mass of each constituent can be quantified to assess the migration and attenuation processes under natural conditions.

This latter approach was used to assess the migration of dissolved benzene, toluene, and the three xylene isomers (BTX) in groundwater in a shallow sand aquifer at Canadian Forces Base Borden, Ontario. These organics are all relatively soluble in water and are common constituents of refined petroleum products such as gasoline. In water supplies they are of concern both for public health reasons (benzene and toluene are EPA priority pollutants) and because they impart foul tastes and odours to water at very low concentrations.

THE BORDEN TRACER SITE

The tracer test site is located in a shallow sand pit downgradient of an abandoned landfill at Canadian Forces Base Borden in southern Ontario. A fine to medium grained glacio-fluvial sand extends from the surface to a depth of about 9 m, and overlies a relatively impervious clay. The sand is saturated below a depth of about 0.5 m to 1.0 m, forming an unconfined aquifer at the site. The lower 3 m to 4 m of the aquifer is occupied by an anoxic leachate plume from the nearby landfill, while the upper 5 m is unaffected by the leachate and is aerobic, containing 2 mg/L to 10 mg/L dissolved oxygen. The sand exhibits significant small scale horizontal bedding, and has a low organic carbon (0.02%), silt, and clay content (Patrick et al., 1985).

The upper five metres of the aquifer is instrumented with a dense array of teflon multilevel piezometers installed for a previous injection experiment (Mackay et al., 1983). The piezometers are placed at 1 m to 3 m intervals on a regular grid pattern, and extend approximately 50 m downgradient from the original injection site. Each multilevel typically consists of fourteen 0.003 m diameter teflon tubes affixed to a common 0.013 m diameter PVC centre stalk. The tube ends are screened, and spaced vertically every 0.2 m. The multilevels are easily sampled using a manifold system described by Mackay et al. (1983). A peristaltic pump creates a common vacuum enabling sample collection from up to fourteen tubes at a time. The samples are retrieved in 18 mL sealed glass hypovials leaving no entrapped air space.

For the present study, a single 0.051 m diameter PVC injection well screened from 2.2 m to 2.8 m was installed within the sampling network. Several additional multilevels containing either 7 or 23 polyethylene tubes were also installed in the vicinity of the injection well to improve the sampling density of

the network. A schematic showing the injection well and the various types of multilevels at the site is presented in figure 1.

THE BTX INJECTION, SNAPSHOT SAMPLING, AND ANALYSIS

A continuous flow system was used for the BTX injection. A spike solution of BTX and chloride was metered into and mixed with groundwater pumped from a 2000 L reservoir, and the dilute solution was injected through a single well into the aquifer. The entire system was sealed to inhibit volatilization losses. The injection began on August 9, 1984 and continued for 21 hours at a flow rate of 1.4 L per minute producing a total slug input of 1800 L. The injection water was sampled every fifteen minutes at the well. Average chemical concentrations were determined to be 2360 µg/L benzene, 1750 µg/L toluene, 1080 µg/L p-xylene, 1090 µg/L m-xylene, 1290 µg/L o-xylene, and 1280 mg/L chloride.

The entire slug of constituents was sampled three days following the injection, and at approximately monthly intervals thereafter for four months. Each sampling session was completed within one to two days providing a three-dimensional 'snapshot' of the organic and chloride plumes. Since the injection, over 3,200 samples have been collected and analyzed. All water samples for BTX analyses were retrieved in full 18 mL hypovials and, with the exception of the first snapshot, were preserved with 0.1 mL of 10% sodium azide and stored in cooler until laboratory analysis. Sodium azide was added to inhibit microbial activity after it was observed that complete losses of BTX could occur within 4 to 6 days due to biodegradation at storage temperatures of 4°C.

In the laboratory, the organic samples were solvent extracted within the hypovials using modified methods described by Mackay et al. (1983) and Glaze et al. (1983). Using separate syringes, one mL of sample was removed and 0.5 mL of

hexane containing m-fluorotoluene as an internal standard was added to each vial. The vials were shaken and allowed to stand for at least ten minutes prior to injection into either a model 5790 or 5840 Hewlett-Packard gas chromatograph equipped with a Supelcowax 10 column (0.32 mm id., 60 m length, 0.25 μm stationary phase thickness) and a flame ionization detector. Sample run times were rapid (5 minutes) and excellent resolution of all constituents was obtained. Detection limits for each constituent were about 1 μg/L. Details of the procedure are described by Patrick et al. (1985).

Prepared standards having approximately 85 μg/L of each organic were run every tenth sample for laboratory quality control, and a limited number of field replicates were also analysed to assess overall precision. With the exception of the first snapshot data, the percent relative standard deviation for both the laboratory standards and field replicates was approximately 5% for each organic and chloride, and the biases of the laboratory standards from the true values were generally $\pm$ 5%. Results from the first snapshot session were considerably poorer, most likely because azide was not added as a preservative to those samples.

RESULTS AND DISCUSSION

HORIZONTAL MIGRATION

Early attention was focused on defining the horizontal aspect of the plumes using vertically averaged concentrations of each constituent at each multilevel piezometer. Two dimensional contour plots of the averaged data were produced using a computerized contouring routine (Surface II). During execution, the averaged concentration data were interpolated to a regular dense grid and then plotted. The grid of values was stored for later use to assess retardation of the organic plumes.

Background chloride concentrations were generally 1 mg/L or less. Background BTX concentrations were below the detection limit, although corrections were required for data from the polyethylene multilevel piezometers. Polyethylene was found in the laboratory to reversibly sorb significant quantities of BTX. In addition, it was observed that dissolved BTX can be transferred through the tubing wall to sample water, and that this continues to occur after several flushings with fresh water. The samples at the polyethylene multilevels thus showed the false presence of BTX at locations below the BTX plumes. This effect was not observed at adjacent teflon multilevels. Corrections to the data were made by eliminating the suspect data points. In any event, the difference between estimates of total mass of BTX in the ground, based upon the corrected and uncorrected data was approximately 5%.

Plots showing the background corrected chloride, benzene, and toluene plumes at 3 days, 53 days, and 108 days after injection are presented in figure 2. Chloride behaves conservatively and therefore illustrates only the effects of advection and dispersion on solute transport. The total mass of the chloride is constant through time. Apparent changes in mass are small, and are a function of the changing density of the sampling network, as well as a result of the effects of dispersion. As shown in figure 2, dispersion is dominant in the direction of groundwater flow producing an elongated plume, with relatively little lateral dispersion. This observation is consistent with the results of a previous tracer experiment in the Borden study area described by Sudicky et al. (1983).

All of the organic species exhibited some loss of mass through time. This is clearly illustrated in figure 2 for toluene, which apparently lost over 90% of its mass within four months. Similar losses were observed for the other hydrocarbons, although benzene, also shown in figure 2, appeared to be affected the least.

These types of mass losses can result from a number of processes, including chemical and biological transformations, volatilization, and irreversible sorption. Chemical transformations of BTX are not reported to occur at significant rates under the range of conditions present in the aquifer. Losses due to volatilization can occur at the water table (Schwille, 1981), although they were prevented during the study by injecting the BTX well below the water table out of contact with the soil gas phase. The mass losses were likely due to biological transformations, although irreversible uptake by the soil remains a remote possibility. Biological transformations of BTX compounds by microorganisms are known to occur in aerobic soil and water environments, including groundwater (Jamison et al. 1976), and the biochemical processes of the transformations are well understood (Hopper, 1978; Gibson et al., 1968). Dissolved oxygen levels were generally at least 0.5 mg/L throughout the plumes over the four months of monitoring.

SORPTION

Sorption of dissolved constituents by soil is a process in which the species are partitioned between solid and aqueous phases. The effect of sorption is to retard the velocity of a species relative to that of the groundwater. For organics, the amount of solid organic carbon in soil is especially important in determining the extent to which sorption will occur, particularly when the dissolved species are non-polar and hydrophobic, and when the soil has a low clay content and an organic carbon content greater than about 0.1% (Karickhoff et al., 1979; Karickhoff, 1984).

In general, the more hydrophobic an organic compound is, the stronger the sorption process will be. The degree of hydrophobicity can be estimated using parameters such as water solubility or the octanol-water partition coefficient.

This has formed the basis of a number of predictive sorption equations which have recently been reviewed by Karickhoff (1984).

In the Borden sand both the clay mineral content and the organic carbon content are low. One would therefore predict compounds such as BTX, which relatively are only moderately and hydrophobic, to sorb very little. Insignificant sorption was previously observed for four different organic tracers in Borden sand (Sutton and Barker, 1985). In that a study, mass losses through time were attributed to biological transformations.

In a tracer study, sorption can be estimated by measuring the average velocity of the centre of mass of the sorbing species, $\bar{v}$, relative to that of a non-reactive species such as chloride, $\bar{v}c$. Sorbed species will be retarded in proportion to the degree to which they partition between the solid and aqueous phases. The retardation factor, R, is defined by the ratio, $\bar{v}:\bar{v}c$ and can, with certain assumptions, be directly included in the classic advection-dispersion equation to account for sorption (Bear, 1979; Freeze and Cherry, 1979).

Retardation factors were determined for BTX from the vertically averaged snapshot data. Centres of mass of each constituent were first estimated using the methods of Freyburg (1984), and velocities were then calculated between snapshots. The effects of continuous mass losses of BTX through time do not appear to have affected the retardation process. Retardation factors calculated between the first and last set of snapshot data are presented in Table 1. Benzene was the least retarded, with a relative velocity (1/R) to that of chloride of about 80%, while the xylenes were the most retarded with relative velocities of about 70%.

As a comparison, retardation factors were calculated using the regression equation of Schwarzenbach and Westall (1981), which correlates sorption with the octanol-water partition coefficients of organic species. Their equation was

Table 1: Retardation Factors, R, for BTX in Borden Sand

Constituent	Predicted R*	R from Tracer Study
Benzene	1.1	1.2
Toluene	1.2	1.2
O-xylene	1.4	1.4
P-xylene	1.5	1.4
M-xylene	1.6	1.4

* from equation of Schwarzenbach and Westall, 1981.

selected because data for methylated benzenes are included in the correlation. A soil organic carbon content of 0.02%, a porosity of 38%, and a bulk density of 1.7 gm/cm^3 were used. These values were previously established as characteristic of Borden sand (Patrick et al., 1985; Sudicky et al., 1983). The predicted retardation factors are given in Table 1. The tracer results and predicted values compare remarkably well, particularly when one considers the uncertainty associated with the correlation equation, and the probable uncertainty in determining the soil organic carbon content. The agreement suggests that the correlation equations may be useful in predicting sorption for certain organic species in soils with organic carbon contents less than 0.1%.

VERTICAL DISTRIBUTION OF BTX

To assess the vertical distribution of BTX in the aquifer, the concentrations were examined in detail at a single multilevel piezometer. A continuous undisturbed core of aquifer sand had been obtained prior to its installation. The multilevel was located approximately 3 m downgradient of the injection well. In the laboratory the core was divided into 0.05 m lengths, and hydraulic conductivities were determined for each length using a falling head permeameter test (Freeze and Cherry, 1979). A profile of the vertical hydraulic conductivity is presented in figure 3 together with depth profiles of chloride and p-xylene concentrations at 32 and 53 days after the injection.

In the hydraulic conductivity profile, contrasts of up to an order of magnitude are evident over distances of only a few centimeters. These contrasts are a result of the thin horizontally layered structure of the sand. The average layer thickness is about 0.01 m.

The chloride concentration profile at 32 days appears erratic, although a plausible interpretation can be made, based upon the hydraulic conductivity profile. The concentrations shown in figure 2 are high in layers having a conductivity of about 1×10^{-4} m/s, and are reduced in layers having lower (0.5×10^{-4} m/s) and higher (2.0×10^{-4} m/s) conductivity. This suggests that chloride had not yet arrived in the low conductivity layers, but had already passed through the profile in the high conductivity layers. To test this idea, the chloride profile was examined at a later time (51 days), and the profile of the retarded species, p-xylene, was examined at both times.

The chloride profile at 53 days is somewhat the reverse of that at 32 days. Chloride concentrations are relatively high in the low conductivity layers, and are low in all other layers. The chloride plumes had apparently passed through the profile at 53 days in all but the least conductive layers.

The concentration of p-xylene at 32 days is high only in the high conductivity layer, where chloride is absent. Because p-xylene is a retarded species it should appear at a later time than the chloride. It is likely, therefore, that chloride in this layer had already passed through the profile at 32 days, as was previously suggested. By 53 days, p-xylene is absent from the high conductivity layers, but is present in most of the low conductivity layers which chloride occupied at 32 days. The net effect of retardation in individual layers was to produce an apparently erratic concentration profile. The sequence of events was that chloride first entered the profile in a highly conductive layer, and was followed in that layer by the retarded species (eg. p-xylene). This sequence was repeated in other layers of lower conductivity at later times.

According to Gillham et al. (1984) the concentration profiles should become smooth as a result of the vertical diffusion of constituents from layers of high

concentrations to low concentrations. The smoothing effect should be enhanced by heterogeneities in hydraulic conductivity in the horizontal direction. In the present study smooth profiles did not appear to develop with travel distances up to 7 m. Perhaps longer travel distances are required for smoothing to become noticeable.

These results have important implications with respect to the design and implementation of field scale studies of contaminant transport in groundwater. Heterogeneities, such as those produced by horizontal layering, can be important in determining the spatial distribution and migration patterns of dissolved species. For organic compounds, the heterogeneities may include factors such as the non-uniform distribution of the sorbing capacity and biodegradation potential of the soil, as well as small scale contrasts in hydraulic conductivity. This heterogeneity effect may account for some of the inconsistent organic/chloride and organic/organic ratios observed at different depths in multilevel piezometers monitoring a landfill-leachate plume at North Bay, Ontario (Reinhard et al., 1984; Barker et al., 1985). It may be valuable to first define the scale of the soil heterogeneities during the design phase of a study. By doing so, the scale of the investigation (eg. the density of the monitoring networks) can be made compatible with the spatial distribution of the heterogeneities, to yield more reliable and comprehensive information.

CONCLUSIONS

The results of the natural gradient tracer study demonstrates that both retardation and mass losses of dissolved BTX constituents can occur in shallow groundwater environments. The losses, which amounted to a reduction of over 90% within less than four months for all constituents but benzene, can be attrib-

uted to aerobic biological transformations. The observed retardation in the velocities of BTX relative to that of chloride were small but significant. Benzene and toluene were least retarded, with relative velocities of about 80% to that of the chloride, while the xylenes were slightly more retarded with relative velocities of about 70%. The retardation is attributed to a reversible hydrophobic partitioning process (sorption) between immobile organic matter in the aquifer and groundwater. As such, the order and the extent of retardation agrees with predictions which are based upon the hydrophobicity of the organics.

Profiles of the BTX and chloride concentrations with depth appeared erratic, predominantly as a result of the differences in hydraulic conductivity among small scale (0.01 m) horizontal layers of the aquifer sand. Retardation was also demonstrated along individual layers, which further contributed to the erratic nature of the profiles. These results suggest that an appreciation of the scale and magnitude of soil heterogeneities in an aquifer can be invaluable in implementing an organic groundwater contamination study, and in evaluating its results.

ACKNOWLEDGEMENTS

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LIST OF FIGURES

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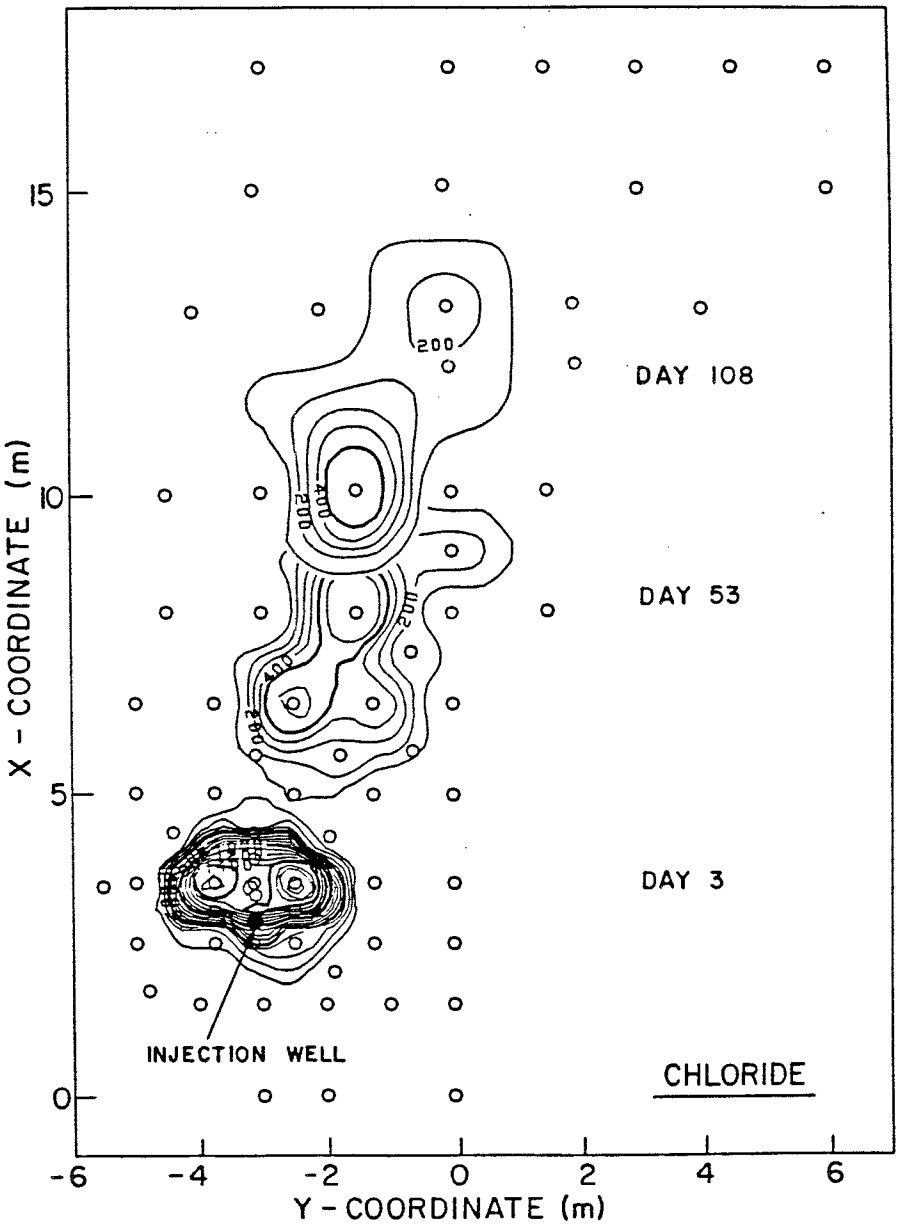
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-6
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0
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600
800
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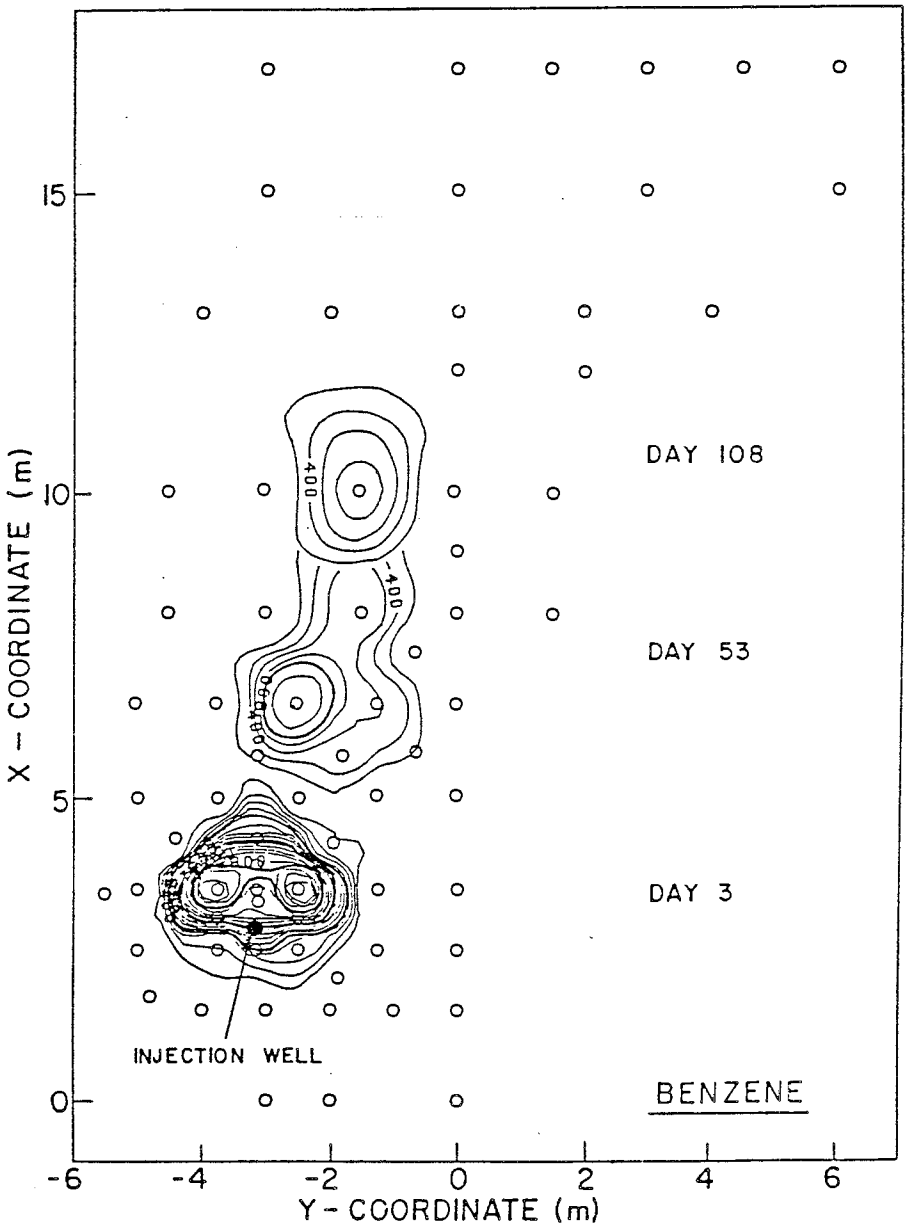
DAY 108
DAY 53
DAY 3
INJECTION WELL
CHLORIDE


15
10
5
0
X - COORDINATE (m)
-6
-4
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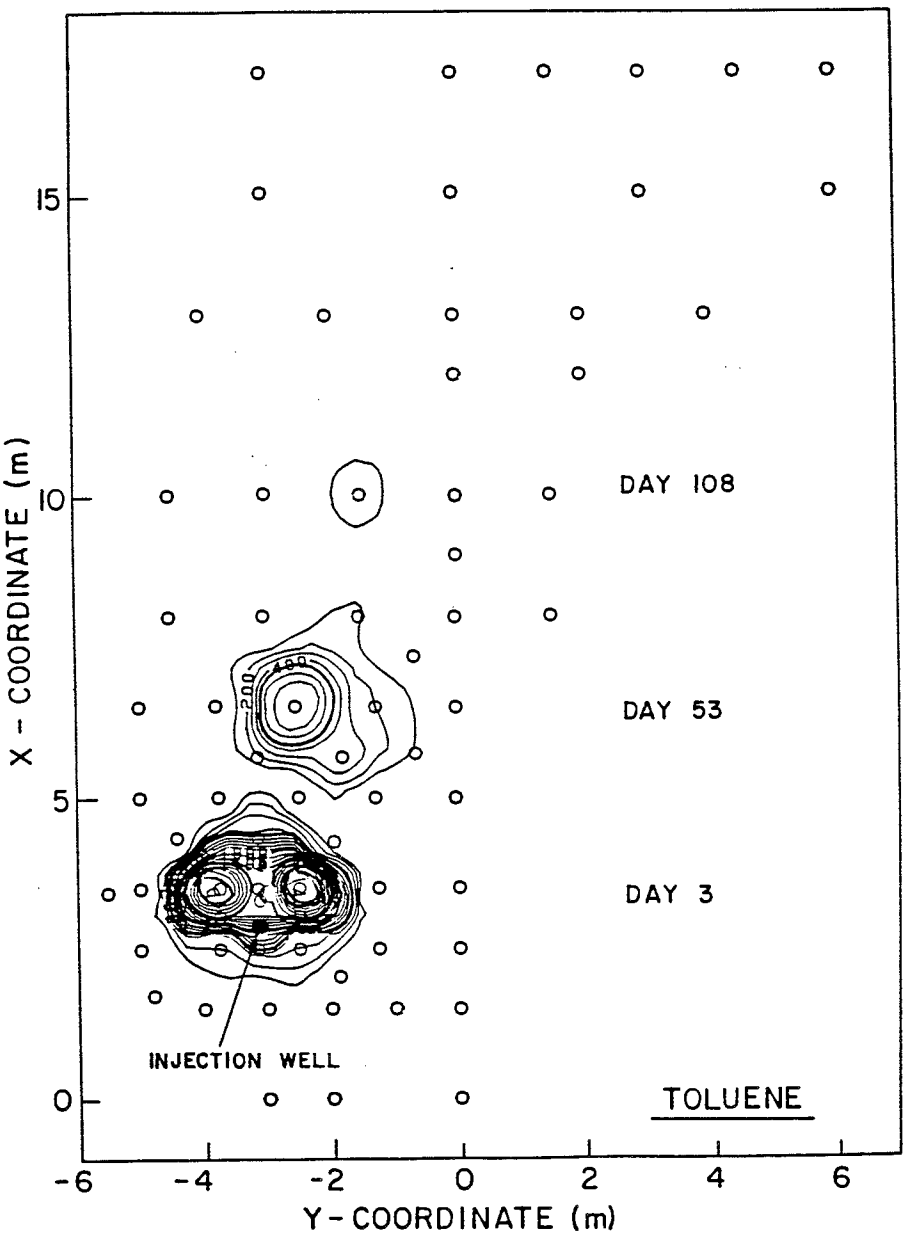
2
4
6
Y - COORDINATE (m)
400
400
DAY 108
DAY 53
DAY 3
INJECTION WELL
BENZENE


15
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5
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X - COORDINATE (m)
DAY 108
DAY 53
DAY 3
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400
INJECTION WELL
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0
2
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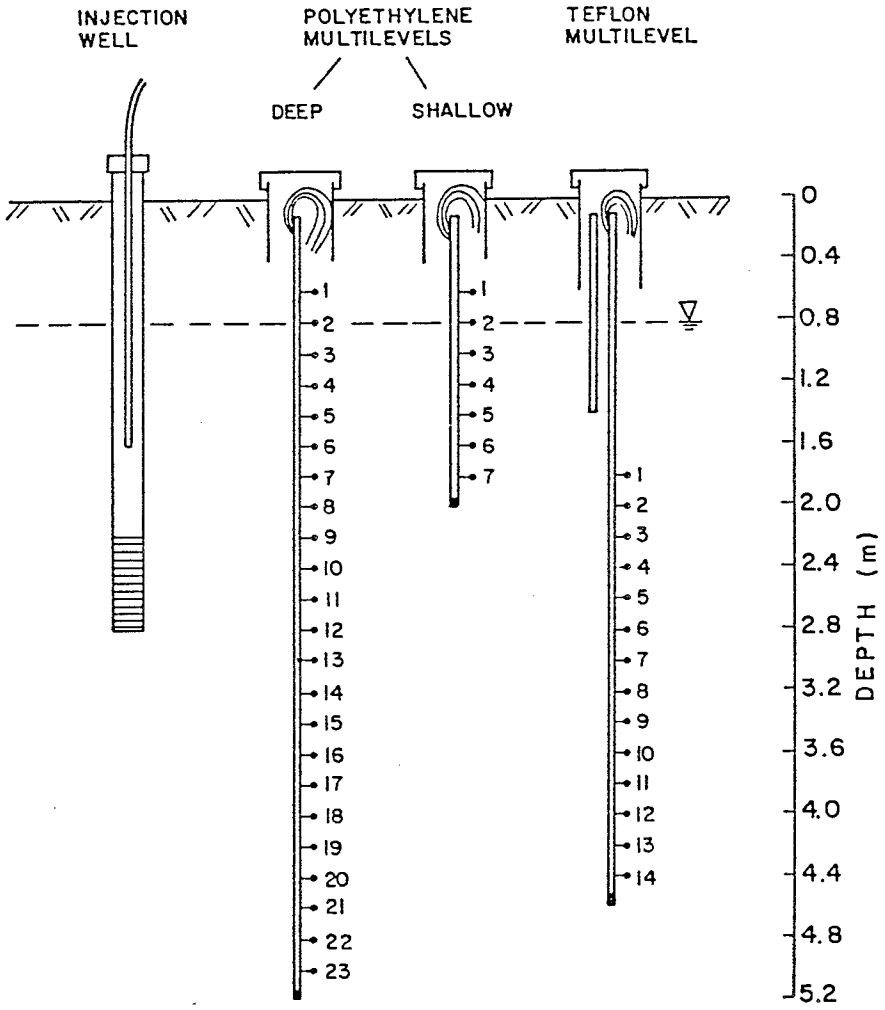
Y-COORDINATE (m)


INJECTION WELL
POLYETHYLENE MULTILEVELS
DEEP
SHALLOW
TEFLON MULTILEVEL
1
2
3
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0.4
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3.2
3.6
4.0
4.4
4.8
5.2
DEPTH (m)

Lecture 2

Behavior of Dense Non-aqueous Phase Liquids, illustrated by lab experiments and conceptual examples.

SUBSURFACE CONTAMINATION BY DENSE NON-AQUEOUS PHASE LIQUID (DNAPL) CHEMICALS

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ABSTRACT

Substances such as many halogenated solvents and PCBs comprise a group of organic chemicals which, in their pure form, can be categorized as dense non-aqueous phase liquid (DNAPL) chemicals. DNAPL chemicals are analogous to petroleum hydrocarbons in that they are immiscible in water, but DNAPL chemicals have densities which are greater than that of water. Approximately one quarter of the organic chemicals on the US EPA List of Priority Pollutants are DNAPL chemicals at typical subsurface temperatures. DNAPL in the subsurface can comprise a very significant source of groundwater contamination.

The potential for subsurface contamination by DNAPL chemicals is significant because large quantities of such chemicals (especially chlorinated solvents) are used in many parts of our modern society. The occurrence of spills during production, transportation and utilization is virtually inevitable. Although DNAPL chemicals are immiscible in water, their solubilities (typically 100 to 5000 mg/L) can often be many orders of magnitude higher than their respective drinking water standards. The combination of immiscibility and high density enables DNAPL released to the subsurface to penetrate downward as a separate non-aqueous phase through both the vadose (unsaturated) zone and the groundwater (saturated) zone. The tendency for DNAPL chemicals to sink through the groundwater zone differs from that of petroleum hydrocarbons which will float on the groundwater zone due to their lower density. In the subsurface, small but significant quantities of chemicals can be dissolved by the groundwater in contact with the DNAPL and can result in groundwater contamination. For many chemicals, the dissolved contaminants derived from the DNAPL can be highly mobile in groundwater because they are not strongly sorbed on geological materials or attenuated by chemical or biological degradation.

The presence of DNAPL chemicals in the subsurface in the form of residual concentrations retained on the soil or rock, or as pools of pure product will have enormous implications with regard to the investigation and control of groundwater contamination at chemical spill sites and waste disposal facilities. The migration of dissolved chemical plumes from DNAPL sources may be contained or controlled by other remedial measures, but groundwater contamination cannot be eliminated in the long-term without removal of the DNAPL source. Where shallow DNAPL sources can be located adequately and are accessible, it may be possible to remove the DNAPL sources by excavation. In most situations, excavation of the DNAPL source will not be not possible. At the present time, there are no methods available which have been demonstrated to be effective in field situations for the removal of DNAPL sources from the subsurface. Further research is needed to develop such methods in order to provide long-term solutions to groundwater contamination problems from DNAPL chemicals. Regulatory agencies and industry must recognize the unique and exceptionally difficult nature of the problem posed by DNAPL chemicals in the subsurface in order to avoid futile or ill-conceived attempts to achieve aquifer cleanup.

INTRODUCTION

Substances such as many halogenated solvents, halogenated benzenes, phthalate esters and polychlorinated biphenyls (PCBs) comprise a group of organic chemicals which in their pure form can be categorized as dense non-aqueous phase liquid (DNAPL) chemicals. DNAPL chemicals are analogous to petroleum hydrocarbons in that they are immiscible in water, but unlike petroleum hydrocarbons, DNAPL chemicals have densities which are greater than that of water. Approximately one quarter of the organic chemicals on the United States Environmental Protection Agency (US EPA) List of Priority Pollutants are DNAPL chemicals at typical subsurface temperatures.

In addition to the chemicals which in their pure form comprise DNAPLs, mixtures of chemicals can also comprise DNAPLs. For example, coal tar or creosote is a complex mixture of polycyclic aromatic hydrocarbons (PAH) such as naphthalene, anthracene and phenanthrene, and various phenols and methylated phenols. The individual PAH compounds are solids at typical subsurface temperatures and the phenols are less dense than water, but the creosote mixture has the characteristics of a DNAPL.

The potential for groundwater contamination by DNAPL chemicals is significant because very large quantities of the chemicals are produced, transported and used in many parts of our modern society. Table 1 shows the 1986 U.S. production of selected organics chemicals which can be categorized as DNAPL chemicals. Production quantities range up to several billion kilograms per year.

Although DNAPL chemicals are immiscible in water and have relatively low solubilities in water (typically 100 to 5,000 mg/L), their solubilities can often be many orders of magnitude higher than their respective drinking water standards (See Table 2).

It was only recognized in the late 1970's that dissolved concentrations of organic chemicals in groundwater used for drinking water could result in taste and odor problems and potential health risks. Carbon tetrachloride, chloroform, 1,2-dichloroethylene and trichloroethylene are known or suspected carcinogens, and exposure to compounds such as carbon tetrachloride, 1,2-dichlorobenzene and tetrachloroethylene can result in kidney and liver damage.

Because drinking water standards for many DNAPL chemicals are so low, small quantities can result in large-scale groundwater contamination problems. For example, 7 L or 10 kg of trichloroethylene (TCE) could potentially contaminate 10^8 L of groundwater to a concentration of 0.1 mg/L or 20 times the drinking water standard of 0.005 mg/L currently proposed by the US EPA. In a sand aquifer, this volume of contaminated ground water would represent a plume 50 m in width, 10 m in depth, and 670 m in length.

The potential for groundwater contamination by DNAPL chemicals is also significant because of their distinctive physical and chemical properties. As previously noted, DNAPL chemicals are immiscible in water and have densities greater than water and, in addition, many have viscosities less than water (See Table 2).

The combination of low solubility, high density and frequently low viscosity enables DNAPL released into the subsurface to penetrate downward into the subsurface through the vadose (unsaturated) zone and/or groundwater (saturated) zone as a separate non-aqueous phase. The tendency for DNAPL chemicals to sink through the saturated zone differs from that of petroleum hydrocarbons which will float on the groundwater in the saturated zone due to their lower densities. In the subsurface, small but significant quantities of chemicals can be dissolved by groundwater in contact with the DNAPL and can result in groundwater contamination.

TABLE 1. 1986 U.S. production of selected organic chemicals which can be categorized as DNAPL chemicals.

	(10^6 lb.)	(10^6 kg)
1,2-Dichloroethane	13,700	6,215
1,1,1-Trichloroethane	600	272
Tetrachloroethylene	425	193
Methylene chloride	420	190
Carbon tetrachloride	415	188
Chloroform	330	150

From American Chemical Society (1987).

TABLE 2. Physical / chemical properties and drinking water standards for selected organic chemicals on the US EPA List of Priority Pollutants which are DNAPL chemicals at typical subsurface temperatures.

	Density (g/cm3)	Viscosity (cP)	Vapor Pressure (mm)	Vapor Density Relative to Air	Solubility (mg/L)	Drinking Water/Groundwater Standard or Guideline (mg/L)			
						HWC	US EPA	WHO	NYSDEC
Methylene chloride	1.33	0.44	349	1.89	20,000	-	-	-	0.01
Chloroform	1.49	0.56	151	1.62	8,200	-	-	0.03	0.1
Carbon tetrachloride	1.59	0.97	90	1.51	785	-	0.005	0.003	0.005
Bromoform	2.89	2.07	5	1.05	3,010	-	-	-	0.05
Bromodichloromethane	1.97	1.71	50	1.31	4,500	-	-	-	0.05
1,2-Dichloroethane	1.26	0.84	61	1.19	8,690	-	0.005	0.01	0.001
1,1,1-Trichloroethane	1.35	0.84	100	1.47	720[a]	-	0.2	-	0.05
1,1,2-Trichloroethane	1.44	na	19	1.09	4,500	-	-	-	0.0005
1,1,2,2-Tetrachloroethane	1.60	1.76	5	1.03	2,900	-	-	-	0.0003
1,1-Dichloroethylene	1.22	0.36	590	2.54	400	-	0.007	0.0003	0.0009
Trans-1,2-dichloroethylene	1.26	0.4	326	2.01	600	-	-	-	0.05
Trichloroethylene	1.46	0.57	58	1.27	1100	-	0.005	0.03	0.005
Tetrachloroethylene	1.63	0.90	14	1.09	200	-	-	0.01	0.002
1,2-Dichloropropane	1.16	na	42	1.16	2,700	-	-	-	0.05
Chlorobenzene	1.11	0.80	12	1.05	488[a]	-	-	-	0.02
1,2-Dichlorobenzene	1.31	1.41	1.0	1.01	100	-	-	-	0.0047
1,3-Dichlorobenzene	1.29	1.08	2.3[a]	1.01	123[a]	-	-	-	0.02

na - No data available. Properties at 20°C.

[a] - Properties at 25°C.

Data from Schwille (1988), Callahan et al. (1979) and Dean (1979).

- No standard designated.

HWC- Health and Welfare Canada US EPA- United States Environmental Protection Agency WHO- World Health Organization
NYSDEC- New York State Department of Environmental Conservation

CASES OF GROUNDWATER CONTAMINATION BY DNAPL CHEMICALS

The principal documented occurrences of groundwater contamination by DNAPL chemicals have resulted from leaks or spills of chemicals from manufacturing facilities and from leakage from chemical waste disposal facilities.

Prior to the 1980's, there was little appreciation of the behavior of DNAPL chemicals in the subsurface. One of the earliest cases in which DNAPL chemicals were recognized to have penetrated into the groundwater zone was at an electrical transformer manufacturing facility in Regina, Saskatchewan (National Research Council of Canada, 1980; Schwartz *et al.*, 1982). Askarel, a mixture of polychlorinated biphenyls (PCB) and trichlorobenzenes (TCB) with a density of 1.4 to 1.5 g/cm^3, was found to have penetrated downward through water-saturated granular fill and fissured clay and silt strata. Comparable behavior was reported at a PCB storage site in Ontario (Golder Associates, 1987), where the PCB liquids migrated through 4 to 5 m of fissured clay and penetrated into fissured dolostone bedrock.

Groundwater contamination from DNAPL chemicals has been reported at several chemical waste disposal facilities in the Niagara Falls area of New York State. At the Hyde Park and S-Area disposal sites, mixtures of organic chemicals consisting primarily of halogenated benzenes and chlorinated solvents (estimated density 1.5 g/cm^3) have penetrated into the subsurface through fissured dolostone bedrock (Guswa and Faust, 1984; Clarke and Kay, 1984). The occurrence of DNAPL chemicals at the sites in the Niagara Falls area was first recognized in the early 1980's, and it was at these sites that the term NAPL or DNAPL was first applied. However, much of the information regarding these sites and the behavior of DNAPL was the subject of litigation and did not start to appear in the open scientific literature until the mid-1980's.

During the early 1980's, it became evident that nature of groundwater contamination at large number of coal gasification plants and wood-preserving plants by coal tar and creosote (density 1.02 to 1.1 g/cm^3) was largely influenced by the behavior of these chemicals as DNAPLs (Villaume, 1985).

The DNAPL chemicals which are probably the most significant with respect to groundwater contamination problems are the chlorinated solvents. In a survey of groundwater monitoring data from 183 hazardous waste sites in the United States, it was found that 4 of the top 5 and 10 of the top 20 most frequently identified organic chemical contaminants were chlorinated solvents (Plumb and Pitchford, 1985). Trichloroethylene, methylene chloride, tetrachloroethylene and 1,1-dichloroethane are included in the top 5 most frequently identified contaminants. Despite their prevalence as groundwater contaminants, there have been few reports in the open scientific literature on DNAPL solvents at sites of groundwater contamination. Dakin and Holmes (1987) recognized the behavior of 1,2-dichloroethane (ethylene dichloride) as a DNAPL following a spill from a train derailment in British Columbia. Although there have been few cases documented at the present time the authors have, in recent years, become aware of a large number of industrial sites and waste disposal sites across North America (particularly those investigated under Superfund in the United States) at which DNAPL solvents are the key contributors to groundwater contamination. Most of this information is buried in the files of regulatory agencies.

It is evident from the preceding examples that DNAPL chemicals result in very significant subsurface contamination problems at many sites and may be important, but yet unrecognized, sources of contamination at great many other sites. However, there have been few studies which have considered in detail the movement of such chemicals in the subsurface and the development of groundwater contamination from such sources. Consequently these processes are not adequately understood.

GROUNDWATER CONTAMINATION BY DNAPL CHEMICALS

Pioneering research on the behavior of DNAPL chemicals in the subsurface was conducted starting in the mid-1970's by Dr. Friedrich Schwille at the Federal Institute of Hydrology in Koblenz, Federal Republic of Germany. Schwille's work has primarily involved small-scale and large-scale laboratory observations of DNAPL penetration into unsaturated and saturated granular geologic materials. Unfortunately, until recently, little of this research was published in English and was largely unknown in North America. Two English summary papers describing the conceptualization and laboratory simulation of DNAPL movement in the subsurface are Schwille (1981) and Schwille (1984). Schwille (1981) was the first English language paper in the open scientific literature to present the concept of heavier-than-water solvents sinking through the groundwater zone. A comprehensive report on Schwille's research entitled "Volatile Chlorinated Hydrocarbons in Porous and Fractured Media- Model Experiments" prepared (in German) in 1984, was translated by Dr. James Pankow of the Oregon Graduate Center and is to be published in 1988 by Lewis Publishers, Inc. of Chelsea, Michigan. Some of the concepts of DNAPL behavior in the subsurface are also described by Villaume (1985).

Based on the work of Schwille and our observations at many chemical spill and waste disposal facilities in North America, four general conceptualizations for the development of groundwater contamination from DNAPL can be described (Figures 1, 2, 3, and 4). In these conceptualizations, a quantity of DNAPL chemical is introduced into the aquifer such as might occur due to a chemical spill or disposal of liquid waste at a waste disposal site. In such situations where the volume of the release is sufficient to overcome capillary resistance in the formations, DNAPL could penetrate downward through the vadose zone (unsaturated zone) and the groundwater zone (saturated zone) due to its high density.

In Figure 1, all of the DNAPL forms a residual in the vadose zone because the input volume does not exceed the retention capacity of the vadose zone. Within this residual zone the DNAPL is present as immobile unconnected and partially connected blobs and filaments. The few data available on residual contents of DNAPL chemicals in unsaturated soils indicate DNAPL contents of 3 to 30 L/m^3 or 1 to 10% of the pore space in sandy soils (Schwille, 1984; F. Schwille, personal communication). Residual contents are higher in the finer grained soils. Such residual contents are comparable to the residual contents typically observed for petroleum hydrocarbons (Wilson and Conrad, 1984).

In situations where DNAPL exists in the vadose zone, groundwater contamination develops when water that infiltrates through the residual zone carries dissolved DNAPL-derived contaminants to the water table. As infiltration of precipitation occurs from time to time, a plume of dissolved contaminants develops in the groundwater zone. Because of the high vapor pressure and high molecular weight of many DNAPL chemicals (primarily chlorinated solvents), the soil air in contact with DNAPL may acquire vapor concentrations sufficiently high to result in density-induced sinking of chemical vapors downward to the saturated zone. In addition, diffusion will result in lateral migration of vapors through the vadose zone. Although at this time the degree of vapor sinking and lateral spreading is not known, it is likely that these mechanisms could result in significant groundwater contamination. Because of vapor transport mechanisms, DNAPL in the vadose zone beneath buildings, parking lots and other surface covers can result in groundwater contamination even though there is no infiltration of water through the DNAPL zone.

In Figure 2, the input volume of DNAPL is sufficiently large for excess DNAPL to move into the groundwater zone but not large enough for an excess to reach the bottom of the aquifer. Groundwater flow patterns will have no significant effect on the movement of DNAPL through the groundwater zone. In laboratory experiments by Schwille (1988) the downward penetration of DNAPL chemicals such as trichloroethylene (TCE) and tetrachloroethylene (PCE) in coarse and medium sand was not noticably affected by horizontal groundwater flow velocities of as high as 14 m/day. The few data available on residual contents of DNAPL chemicals in

FIGURE 1. Groundwater contamination from a residual DNAPL source in the vadose zone.

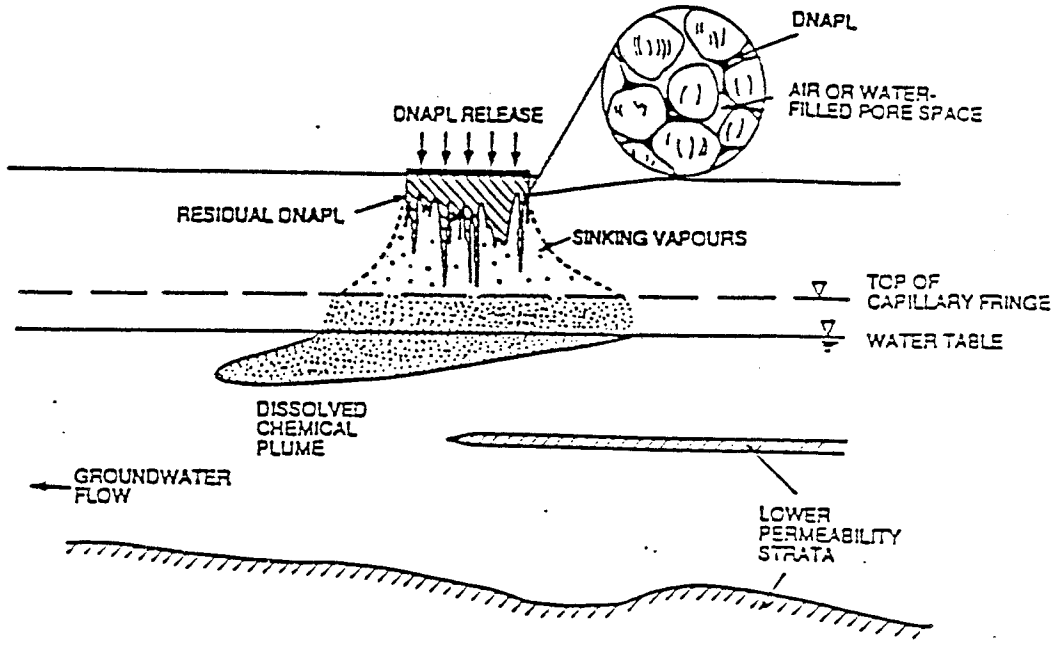
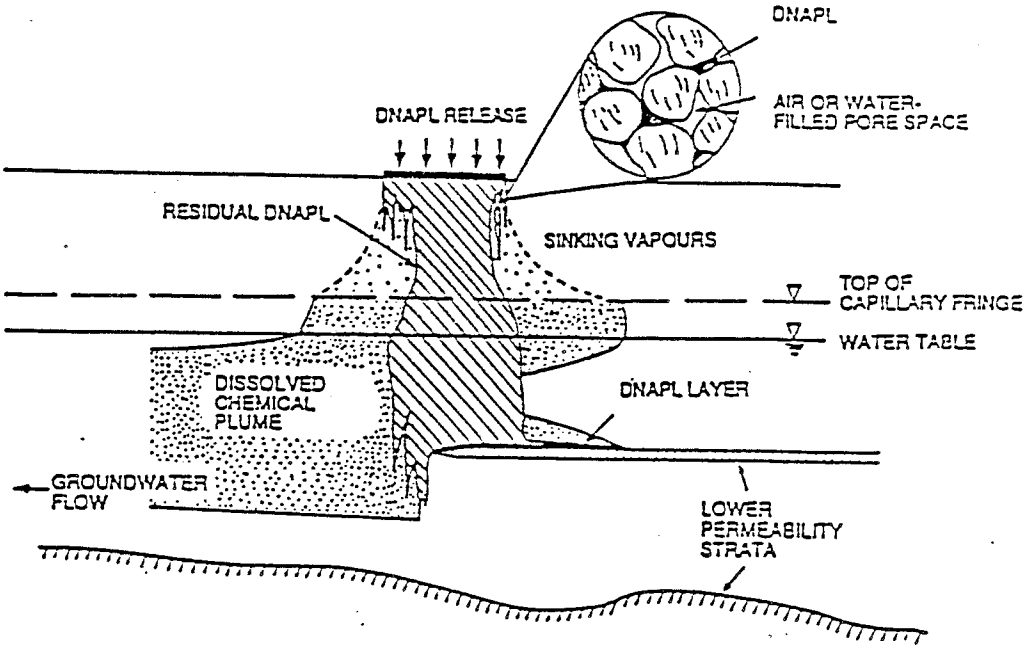


FIGURE 2. Groundwater contamination from residual DNAPL source in the zadose zone and the groundwater zone.



saturated soils indicate DNAPL contents of 5 to 50 L/m^3 or 2 to 15% of the pore space in sandy soils (Schwille, 1984; F. Schwille, personal communication). Residual contents are higher in the finer grained soils. The presence of DNAPL in the pore space in the residual zones does not significantly affect the permeability of these zones to groundwater flow.

Dissolved contaminants derived from the residual DNAPL in the vadose zone and residual DNAPL in the groundwater zone cause a contaminant plume to develop. In small-scale laboratory experiments, groundwater in contact with DNAPL quickly (minutes to hours) acquires dissolved concentrations approaching the solubility of the DNAPL (Pfannkuch, 1984; Anderson *et al.*,1987; Schwille, 1988). However, this condition is seldom observed in field situations, even when monitoring wells are located close to suspected DNAPL source areas. Maximum dissolved concentrations in monitoring wells are typically less than ten percent of the solubility concentrations of the DNAPL. This phenomenon is likely a result of heterogeneous distribution of DNAPL in the subsurface, non-uniform flow of groundwater through and around the residual DNAPL zones and pools, and the tendency for blending or mixing of groundwater from various depths during sample collection from monitoring wells.

If the volume of spilled DNAPL is larger than the retention capacity of the vadose and groundwater zones, a portion of the DNAPL will settle out as a pool of free liquid on the bottom of the aquifer as shown in Figure 3, or it will settle out on the first low permeability bed in the aquifer. Resistance as a result of capillary forces should inhibit or prevent the movement of DNAPL through finer grained strata. Unless these strata contain discontinuities such as fissures or root holes, or heterogeneities in grain size which allow the downward movement of DNAPL, fine grained strata should form a barrier to DNAPL migration. DNAPL may form puddles or pools in depressions on such confining strata. In situations where the confining stratum is sloped, DNAPL can continue to move downslope and its movement need not be controlled by the direction of groundwater flow. Depending on the volume of the spill and the configuration of confining strata, DNAPL may move substantial distances laterally away from the area in which it was released.

The rate of DNAPL infiltration into the subsurface may be extremely rapid. For example, in laboratory experiments conducted by Schwille (1988) in coarse-grained sand, tetrachloroethylene (PCE) penetrated through a 60 cm thick unsaturated zone in 10 minutes and a 90 cm thick saturated zone in 60 minutes.

DNAPL chemicals can also penetrate into fractured rock as shown in Figure 4. The pattern of DNAPL movement will be controlled primarily by the orientation and interconnection of fractures. Based on laboratory experiments by Schwille (1988), there will be little DNAPL retained on the fracture surfaces as residual either above or below the water table. For planar fractures of 0.2 mm aperture, Schwille estimated the residual retention to be less than 0.05 L/m^2. For a weakly fractured rock of moderate hydraulic conductivity with a fracture frequency of 5 fractures per metre, this retention capacity would represent a residual content of approximately 0.25 L/m^3, substantially less than the residual contents for soils. Therefore, for a given volume of DNAPL introduced into the subsurface, contamination in fractured media can can spread to a much greater extent areally and to a greater depth than in porous media.

Many of the dissolved contaminants from DNAPL sources are not strongly influenced by sorption on aquifers solids and are not rapidly removed from the groundwater by chemical or biological degradation. Therefore, in each of these conceptualizations, large plumes of groundwater contamination can develop as groundwater flow carries the dissolved contaminants away from the site. The dissolution of DNAPL from the residual zones and DNAPL pools will continue and a plume of contaminated groundwater will be generated so long as DNAPL remains in the subsurface.

FIGURE 3. Groundwater contamination from residual DNAPL and DNAPL pools.

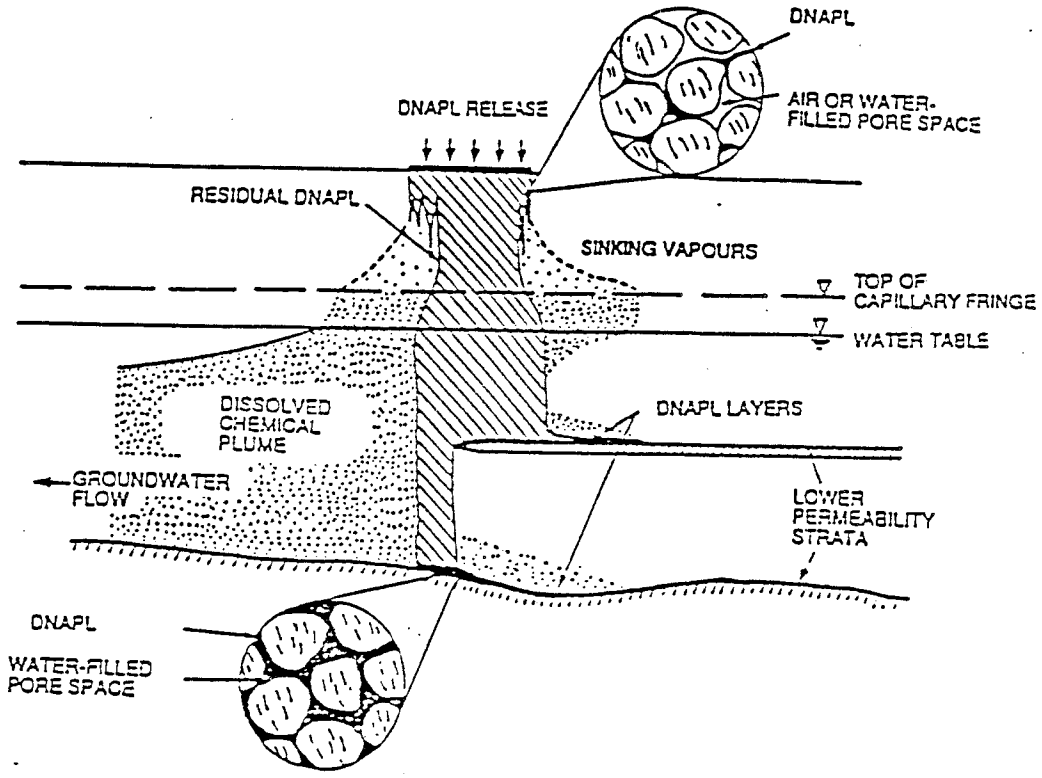
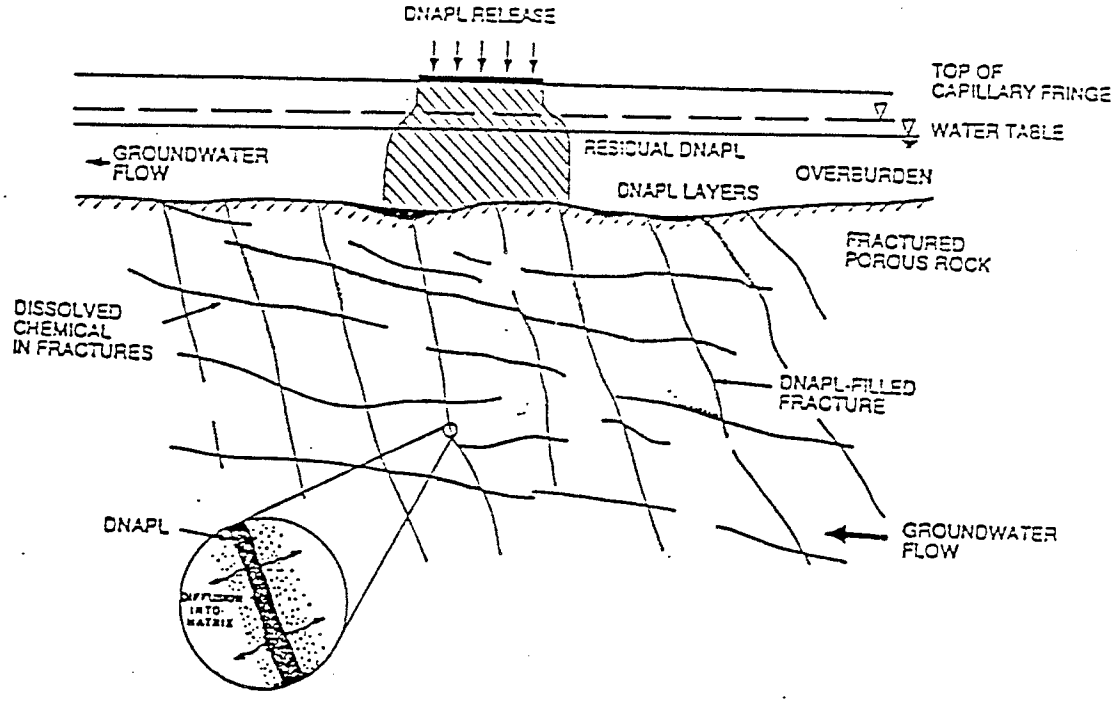


FIGURE 4. DNAPL migration into fractured bedrock formations.



IMPLICATIONS WITH RESPECT TO SITE INVESTIGATIONS AND MONITORING

The presence of DNAPL chemicals in the subsurface has significant implications regarding the interpretation of groundwater contamination patterns at chemical spill sites and waste disposal facilities. The penetration of DNAPL into the subsurface extends the source of groundwater contamination from at or close to the ground surface to a potentially far greater depth. This means that groundwater contamination patterns resulting from a DNAPL source may be significantly different than that which might develop from a near-surface source.

The presence of a DNAPL source may result in the highest concentrations of dissolved chemicals occurring at the base of an aquifer rather than near the top as would be typical of a near-surface contamination source. Similarly, because the movement of DNAPL may be deflected laterally by low permeability strata, the ultimate location of the DNAPL source may be substantially removed from the area of the original release. Lateral vapor transport through the vadose zone may also result in the development of groundwater contamination remote from the area of the original chemical release. Because DNAPL movement and vapor migration will not be controlled by the groundwater flow pattern, groundwater contamination can develop up-gradient and cross-gradient from the area of the chemical release in addition to in the expected down-gradient direction. Therefore, the possible presence of a DNAPL source must be considered in the planning of borehole / monitoring well locations and depths for hydrogeologic investigations at sites where such chemicals have been released to the subsurface.

Significant quantities of DNAPL chemicals can be contained in residual zones or pools which are a very small size (ie. distance of several metres). For example, a spill of approximately 800 L of DNAPL could potentially be contained in a pool in sandy soil measuring only 3.0 m by 3.0 m by 0.3 m. Such a quantity of DNAPL could comprise an extremely significant source of groundwater contamination but if such zones are to be identified by borings and monitoring wells, the spacing between borings must be sufficiently small. In general, such spacings would be much smaller than those typically used in hydrogeological investigations of dissolved contaminant plumes. Even in the situation when DNAPL pools are intersected by borings or monitoring wells, special precautions must be taken to ensure that DNAPL will be recovered in the monitor and its presence positively identified. In the majority of situations, the quantity of DNAPL which can move or be induced to move into a boring or monitoring well is relatively small. Because DNAPL will penetrate downward, DNAPL which enters the filter pack of a monitoring well will sink to the bottom of the filter pack. If the monitoring well is set above the bottom of the filter pack, it may not be possible for DNAPL to enter that well and be positively identified. When DNAPL does enter a boring or monitoring well, it will stay at the bottom of the well. The bottom of the well must be carefully sampled in order to recover and identify the DNAPL. In most monitoring installations, silt and fine-grained particulate material collects at the bottom of the well despite well development. The presence of particulate material at the bottom of borings or monitoring wells may make identification of DNAPL more difficult.

A very important consideration in the investigation of sites where DNAPL is present is the possible contamination of the groundwater in deeper strata as a result of drilling through zones of free DNAPL. If a deep boring intersects a pool of DNAPL in a granular media or a zone of free DNAPL in a fractured media, DNAPL can enter the boring during drilling or prior to the installation of monitoring wells. This DNAPL would sink to the bottom of the boring. Only small quantities of DNAPL at the bottom of such borings could result in the detection of significant, but erroneous, concentrations of dissolved contaminants in the groundwater sampled from these deeper levels. When borings are extended downward through DNAPL zones, special precautions must be taken to prevent DNAPL from moving down the boring as drilling proceeds.

IMPLICATIONS WITH RESPECT TO REMEDIAL MEASURES

The presence of DNAPL chemicals in the subsurface will also have enormous implications with regard to remedial measures to control groundwater contamination at chemical spill sites and waste disposal facilities. DNAPL chemicals can potentially penetrate downward into the subsurface to beyond the depth of feasible removal by excavation. Similarly, DNAPL chemicals can also migrate into areas which are otherwise inaccessible such as beneath buildings or process areas. Even where DNAPL is present in the vadose zone beneath buildings, parking lots or other surface covers, groundwater contamination can still result due to sinking vapors and lateral migration of vapors.

Zones of residual DNAPL and DNAPL pools can comprise very significant sources of long-term groundwater contamination unless they are removed, but removal is generally very difficult or not feasible with existing remedial technologies. Simply purging and treating contaminated groundwater from dissolved plumes will not generally be effective in remediating the contaminant source because the residual zones and pools can represent such a large mass of chemical. Consider, for example, a purge well system which recovers groundwater contaminated by TCE with an average concentration of 1000 µg/L and at a rate of 450 L/min. Dissolved TCE concentrations as high as this are encountered at some sites but concentrations are typically only several hundred µg/L in most dissolved solvent plumes. Although seemingly low, such concentrations are many times higher than drinking water standards. Pumping rates of the order of 450 L/min. would be common in many purge well systems. For the system described above, the total amount of TCE recovered would be only 160 L per year or three quarters of a barrel of TCE. If concentrations in the purged groundwater were lower, the amount of TCE recovered would also be lower. For the cost and effort of purging and treating such large volumes of contaminated groundwater, the benefit may be small with respect to depletion of the contamination source.

Studies by Schwille (1988) suggest that the rate of dissolution of DNAPL pools is related almost directly to the rate of groundwater flow over the pool. That is, the higher the groundwater flow rate, the more rapid the mass depletion of the DNAPL source. However, because of their relatively low solubility, most DNAPL chemicals will not be rapidly dissolved by flowing groundwater. Consider, for example, a volume of sandy soil measuring 3 m by 3 m in area by 3 m in depth which contains a bulk residual TCE content of 30 L/m^3. This quantity of TCE would be approximately 800 L or 4 barrels of chemical. Groundwater flows through this zone at a rate of 3 cm/day reflecting rates typical for a sandy aquifer (hydraulic conductivity of 10^{-3} cm/s, a hydraulic gradient of 0.01 and a porosity of 0.3). If TCE dissolves into the groundwater to 10 % of its solubility (110,000 µg/L) approximately 300 years would be required to remove all of the residual DNAPL TCE from the aquifer. Even though the rate of dissolution may be increased by increasing the rate of groundwater flow through the DNAPL zones, in most groundwater environments, groundwater flow rates can only be increased by a factor of 5 or 10 except very close to a pumping well. This means that it is not likely possible to accelerate the dissolution of DNAPL significantly in most field situations. The preceding calculation suggests that DNAPL chemicals can remain in the subsurface and contribute to groundwater contamination for decades to hundreds of years. This conceptual calculation is consistent with the observation that groundwater contamination persists at many sites where chemicals were leaked or spilled many decades ago. Long-term solution of the groundwater contamination from DNAPL sources in the subsurface must be directed at removal of the source.

Conventional methods for the removal of contaminated groundwater or floating non-aqueous phase liquids (ie. petroleum) such as purge wells and collector trenches may not be effective for the removal of DNAPL because the movement of DNAPL is not controlled by the groundwater flow pattern. In porous materials where it is possible to locate pools or zones of free DNAPL in the subsurface, it is found that at most only a small portion of the DNAPL can be removed with recovery wells or collector trenches. Villaume *et al.* (1983) showed that coal tar could be recovered from a gravel stratum in Pennsylvania, but this situation involved a thick (3.5 m)

well defined pool with a chemical of relatively low density (1.02 g/cm^3). In fractured media, experience at a PCB storage site in Ontario (Golder Associates, 1987) and at other sites (Ferry *et al.*, 1986) has shown that although it is possible to recovery small quantities (several litres or less) of DNAPL, recovery rates are slow and it is often not possible to sustain continued recovery. In either case, even following recovery of the free DNAPL, a considerable percentage of the DNAPL will remain in the subsurface as a residual and will continue to be a source of groundwater contamination. The DNAPL in the residual zone is immobile except under extremely high hydraulic gradients (ie. 1 to 10 or more) which can seldom be achieved in near-surface groundwater environments (Wilson and Conrad, 1984).

At the present time, excavation and removal of the contaminated soil is the only method which has been demonstrated to be an effective means of fully remediating DNAPL sources in the subsurface. Excavation is a well recognized remedial measure because it is conceptually simple and potentially capable of complete removal of subsurface DNAPL sources. Successful remediation of DNAPL sources can only be achieved when the DNAPL source can be located and when the DNAPL is accessible using available excavation techniques and equipment. This generally would require that the DNAPL be confined to the vadose zone at a depth of 5 to 10 m or less. At most sites, DNAPL has penetrated to a significant depth or has penetrated into otherwise inaccessible areas such as beneath buildings and into bedrock formations and excavation of DNAPL sources is not effective.

Excavation has been a preferred method of remediation by regulatory agencies because the behavior of DNAPL chemicals and their penetration to greater depths has not been appreciated. When the behavior of DNAPL chemicals is understood, it is apparent that as a method for eliminating groundwater contamination, excavation of DNAPL sources will rarely be worth the high cost of removal and disposal. This may be even more true now that fewer waste disposal facilities are available for materials from the cleanup of groundwater contamination sites. In addition, at sites where the DNAPL chemicals are volatile or the method of excavation could release contaminated particulate material, the emission of contaminants into the air may be of sufficient environmental concern to prohibit excavation.

In areas where removal of the DNAPL by excavation is not effective, the remediation of the residual zones and pools may only be possible by innovative *in situ* removal techniques. Potential options for *in situ* removal methods can include:

- Induced Volatilization
- *In Situ* Biodegradation
- Chemically-enhanced Displacement
- Steam Displacement
- Chemically-enhanced Dissolution

The objective of these *in situ* removal methods is the complete elimination of the DNAPL to the degree that no further significant groundwater contamination will develop from the source area. Because the drinking water standards for most DNAPL chemicals are low and because the mass of chemical represented by a DNAPL source is so high, removal of virtually all of the in-place DNAPL (possibly > 99 %) may be required to meet this objective.

Induced volatilization is a potential method for the removal of volatile DNAPL chemicals from residual zones and pools in the vadose zone. Induced volatilization has also been referred to as vapor extraction, *in situ* soil stripping and soil vacuuming. Induced volatilization would involve increasing the rate of advective gas flow through the soil. This is accomplished by means of a system of vacuum wells to remove the air and volatile chemicals released to the soil gas from the DNAPL. Such systems may also have injection wells to force air into the soil and enhance flow to the vacuum wells. Purge wells may also be used to lower the water table to remove chemicals formerly present in the groundwater zone. Induced volatilization methods have been demonstrated by laboratory and small field-scale experiments and implemented at several field sites for remediation of volatile organic chemicals (many of them DNAPL) and petroleum hydrocarbons (Thornton and Wootan, 1982;

Marley and Hoag, 1984; Agrelot *et al.*, 1985; Zimmermann and Brizgys, 1986; Kolturiak, 1986; Crow *et al.* 1987). Removal of a large portion of the chemicals present in the vadose zone is possible using this method, but at the present time it has not been shown that the method can achieve complete removal of DNAPL sources in actual field situations.

In situ biodegradation methods have been successfully applied to the treatment of petroleum hydrocarbon contaminants in groundwater but they have not been demonstrated to be effective for remediation of subsurface DNAPL sources. Such methods involve the injection of oxygen and other nutrients into the groundwater to stimulate the growth and activity of naturally occurring aerobic bacteria which can degrade the petroleum compounds. However, most DNAPL chemicals are halogenated compounds which are degradable under anaerobic conditions or are resistant to degradation. The degradation of many DNAPL chemicals, when is does occur, is not generally complete to innocuous compounds but rather involves transformations to other equally undesirable chemical compounds. In addition, within the zone of DNAPL residual or pools, the chemical concentrations will be very high and will likely have a poisoning or inhibitory effect on the bacteria performing the biodegradation.

Chemically-enhanced displacement methods are used in the petroleum industry for secondary and enhanced recovery of oil from oil fields. Chemically-enhanced displacement involves the injection of surfactants or other chemical agents into the formation to reduce the interfacial tensions between the non-aqueous phase and the groundwater and allow the non-aqueous phase to be more readily displaced by the flowing groundwater. The addition of surfactants can reduce interfacial tensions by a factor of 1000 times or more (Latil, 1980) and increase potential mobility of the non-aqueous phase by the same order. Although the principles of such methods are well understood and the methods are frequently effective for oil recovery, the methods cannot be directly applied to the cleanup of DNAPL chemicals in the subsurface. Secondary and enhanced oil recovery operations are employed in confined formations which are hundreds to thousands of metres in depth and where very high pressures can be applied by pumping or injection. Similar pressures cannot be exerted in near surface (<50 m) groundwater environments. In addition, many of the surfactant chemicals which could be considered for use in such a recovery scheme, could pose a significant environmental concern in their own right when injected into a near-surface groundwater environment.

Steam displacement is another method used in enhanced oil recovery operations which may be applicable to the remediation of DNAPL sources. Steam displacement would involve the injection of steam through the DNAPL zones and would result in vaporization of the DNAPL to allow recovery of the DNAPL from recovery wells. Hunt *et al.* (1987a and 1987b) have evaluated the theory of steam displacement and performed laboratory experiments demonstrating the potential for the use of steam displacement for remediation of DNAPL sources in the subsurface.

In assessing the potential for the use of enhanced oil recovery methods for the remediation of DNAPL sources, two key factors must be remembered. Firstly, laboratory demonstrations of oil recovery methods invariably show a much higher removal efficiency than can be achieved in a field situation. This is likely due to the heterogeneities in the distribution of the non-aqueous phase and non-uniform groundwater flow patterns which exist in field situations but cannot be simulated in laboratory demonstrations. Secondly, the standard by which enhanced oil recovery is judged to be effective is far different from the standard by which DNAPL recovery methods must be judged. For example, if conventional oil recovery removes 30 % of the oil resident in the formation, enhanced oil recovery operations would be deemed highly successful if they resulted in recovery of an additional 20 to 30 %, still leaving 40 % of the oil in-place. In contrast, in order to significantly reduce or eliminate groundwater contamination emanating from a DNAPL source, it is likely that recovery of virtually all of the in-place DNAPL would be required.

The injection of surfactants or other chemical agents may also act to increase the solubility of the DNAPL in the groundwater. If the solubility of the DNAPL can be increased sufficiently, it may be possible to remove the DNAPL from the subsurface by focusing groundwater flow

through the DNAPL zones. Chemically-enhanced dissolution of PCB and TCB has been evaluated on a laboratory scale. Ellis *et al.* (1985) evaluated the extraction of PCB from soils using several non-ionic surfactants and found removal efficiencies of 92 % using a 1.5 % aqueous solution of the surfactants. Extraction of PCB from the same soils using water alone resulted in removal efficiencies several orders of magnitude lower. General Electric (GE) Company has also evaluated the extraction of PCB Arocior 1260 from soils using anionic and non-ionic surfactants. GE found that 0.1 % to 1.0 % surfactant solutions were capable of increasing the PCB solubility by a factor of 10^5 to 10^6 times. Zenon Environmental Inc. (1986) evaluated TCB solubility in methanol, ethanol and iso-propanol solutions and found that alcohol concentrations of 30 % to 50 % were required to increase TCB solubility by a factor of ten times.

Chemically-enhanced dissolution, although potentially feasible, has not been demonstrated on a field scale. The considerations discussed previously for chemically-enhanced displacement are also applicable to enhanced dissolution. The environmental effect of the co-solvent or surfactant chemicals used should be carefully evaluated. Also, the enhanced dissolution scheme must be designed so that the hydrogeologic conditions together with the groundwater injection and recovery system will provide for complete recovery of the dissolved chemicals. In such a system, the recovered groundwater would have very high concentrations of dissolved or emulsified chemicals and this highly contaminated water must not be allowed to escape the recovery system.

Of the in situ remedial methods described above, only induced volatilization has been developed to the stage where it is being applied at field sites and even this method may not be capable of cleanup to the concentrations levels desired. The other methods are far from being ready to rely on at field sites. Where remedial action is undertaken, at present, conventional engineering approaches are generally being used such as aquifer pumping wells to control off-site migration of dissolved contaminants, and combinations of cut-off walls and source area groundwater pumping. For most DNAPL sites, these measures represent control measures rather than cleanup measures.

CONCLUSIONS

DNAPL chemicals in the subsurface have resulted in groundwater contamination problems at a wide variety of industrial sites and waste disposal facilities in North America. DNAPL chemicals are likely to be key , but yet unrecognized, sources of groundwater contamination at a great many other sites. The low solubility and high density of DNAPL chemicals allow them to penetrate into the subsurface through both the vadose zone and the groundwater zone. This behavior makes DNAPL chemicals a source of groundwater contamination unlike any other.

The presence of DNAPL chemicals in the subsurface has enormous implications with regard to the investigation and remediation of groundwater contamination. The penetration of DNAPL into the subsurface extends the source of groundwater contamination from at or close to the ground surface to a far greater depth. The presence of a DNAPL residual mass or pool at depth may result in the highest concentrations of dissolved chemicals occurring at the base of an aquifer rather than at the top as would be typical of a near-surface source of contamination. The possible occurrence of DNAPL sources must be considered in planning borehole / monitoring well locations and depths at sites where these chemicals have been used in industrial processes, stored, transferred or disposed.

Because of their low solubility and the low drinking water standards for most such chemicals, DNAPL chemicals can persist in the subsurface and cause groundwater contamination problems for many decades or hundreds of years. The migration of dissolved chemical plumes from DNAPL sources may be contained or controlled by other remedial measures, but groundwater contamination cannot be eliminated in the long-term without removal of the DNAPL source. Where shallow DNAPL sources can be located adequately and are accessible, it may be possible to remove the DNAPL sources by excavation. In most situations, excavation of the DNAPL source will not be not possible. At the present time, there are no methods available

which have been demonstrated to be effective in field situations for the removal of DNAPL sources from the subsurface. Further research is needed to develop such methods in order to provide long-term solutions to groundwater contamination problems from DNAPL chemicals. Regulatory agencies and industry must recognize the unique and exceptionally difficult nature of the problem posed by DNAPL chemicals in the subsurface in order to avoid futile or ill-conceived attempts to achieve aquifer cleanup.

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Lecture 3

Field Case Histories on Groundwater Contamination

J-21

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VOLATILE AROMATIC AND CHLORINATED ORGANIC CONTAMINANTS IN GROUNDWATER AT SIX ONTARIO LANDFILLS

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ABSTRACT

Studies of the migration of organic contaminants in shallow aquifers impacted by landfill leachate at six sites in Ontario are reported. Three sites are located on very permeable sand deposits, one on less permeable sand till and two on fractured sedimentary bedrock. The migration rate and persistence of volatile, one-and-two carbon, halogenated hydrocarbons (halocarbons) and volatile aromatic hydrocarbons are emphasized. These compounds are ubiquitous in sanitary landfill leachates and are quite mobile in groundwater. They are at very low concentrations (less than 5ppb each) at the Borden landfill site, where most waste was burned before landfilling.

At the Woolwich site, volatile halocarbons are found at very low concentrations (less than 0.5 ppb each) up to one kilometer from the site, indicating that they may be very mobile and persistent in this aquifer. Attenuation, probably due mainly to dispersion, has resulted in only sub-ppb concentrations persisting beyond two hundred meters of the site.

The contaminant plume at North Bay has been discharging to the surface about eight hundred meters from the site for a number of years. Some mobile volatile organics, therefore, are found throughout the plume. Halocarbons do not persist and some aromatics appear to be undergoing biodegradation as well. For these and other contaminants, dramatic attenuation is observed within the eight hundred meter plume, probably as the result of dispersion.

Groundwater velocities in the less-permeable sand and sand till at the new Borden site are much lower than in the other aquifers, so contaminants have only migrated perhaps two hundred meters laterally. Volatile halocarbons may be migrating at the groundwater velocity, while some retardation of aromatics may be occurring. However, the erratic contaminant distribution complicates the consideration of contaminant migration.

Contaminant distributions are irregular in fractured bedrock at the Bayview and Hamilton sites. The irregular and generally low concentration of halocarbons, coupled with the generally-poor background water quality in these bedrock flow systems, makes the definition of the zone of contamination at these sites very difficult. Although these low-porosity carbonate/shale bedrock systems could distribute leachate contamination through a large volume of rock, it is encouraging to note the rather restricted zone of clearly-impacted groundwater. The major, mobile organic contaminants at the Hamilton site are the volatile aromatic hydrocarbons. Recognition of only-slightly-impacted groundwater at this site is complicated by the occurrence of these organics at ppb levels in apparently uncontaminated, background groundwater.

Temporal variations, over weeks and years, are found for all contaminants at these sites. Input from the landfill appears to be temporally variable and so is a major cause of subsequent variations within the leachate plume. The processes of dispersion, which smoothes such variations at some sites (Borden), does not appear to be effective at damping temporal variability along the plume at North Bay nor in the fractured-bedrock systems.

INTRODUCTION

It has long been recognized that municipal landfills in Ontario and elsewhere produce leachate that causes contamination of groundwater. Zones of contaminated water, termed leachate plumes, can be quite extensive at landfills situated on permeable, geological materials. Since 1976 researchers at the Institute for Groundwater Research have investigated the physical and chemical controls of contaminant migration at such landfill sites. Since 1982 additional emphasis has been placed on the migration of organic contaminants. Some of these organic studies were conducted in collaboration with researchers from the Environmental Engineering Group at Stanford University and from the Department of Environmental Chemistry and Biology at the Oregon Graduate Center.

Six landfill sites are currently being investigated. Three sites (Borden, Woolwich, North Bay) are situated on unconfined sand aquifers, one site (new Borden) on unconfined sand and clay tills, and two sites (Bayview and Hamilton) on fractured sedimentary bedrock. Thus, a wide range of hydrogeological conditions are included in these studies.

Methods of investigation at these sites are summarized by Barker et al. (1984). Essentially, an extensive network of multilevel groundwater sampling devices, termed multilevel piezometers, are established to provide a detailed, three-dimensional picture of contaminant distributions. Hydraulic information obtained by water-level measurement, well-testing, and detailed core analysis defines the groundwater flow system responsible for contaminant migration. Hydraulic testing, piezometer sampling , and laboratory studies of sorption and biotransformation can then be integrated, with the assistance of mathematical simulation when appropriate, to describe the migration of organic contaminants in the plumes.

With respect to organic contaminants, these studies are addressing several questions:

1) what organics are present in landfill leachates?
2) how fast do they migrate in groundwater?
3) how far and for how long do they persist? and
4) what are the processes controlling their migration and persistence?

The fourth question is important to address if the results of these field studies are to be generalized for application to other landfill or waste disposal situations. Only a thorough understanding of the processes will establish a reliable predictive capability.

It is important to study real landfill situations since only in the field are the results of complex, interactive transport processes fully apparent. This complexity, however, also limits our ability to identify the contribution of specific processes, such as sorption, dispersion, and transformation, to organic contaminant migration and persistence. The major field limitations are the undefined history of inputs from the waste to the groundwater and the uncertainties in the flow system hydraulics. Laboratory studies, under conditions representative of field sites, are often more useful to evaluate specific processes. Another approach currently being emphasized at IGR is to conduct field-scale experiments in which solute-spiked groundwater is injected into a well-characterized aquifer and the migration of solutes under natural flow conditions is monitored by sampling from a dense, three-dimensional network of multilevel piezometers. This provides for a well-defined input and a well-characterized flow system in which the processes can be more clearly investigated. "Natural gradient injection" experiments were used by Sudicky et al. (1983) to study dispersion of chloride, by MacKay et al. (1983) for selected halogenated organics, by Sutton and Barker (1985) for selected soluble organics, and by Patrick and Barker (in press) for monoaromatic hydrocarbons. Thus, laboratory and field-scale experiments augment the current studies of organic contaminant migration at landfill sites, all with the aim to better understand the processes controlling organic contaminant behaviour in groundwater.

Table 1 Representative, Highly Impacted Groundwater from Landfill Sites in Southern Ontario.

Landfill	Borden	Woolwich	North Bay	New Borden	Bayview	Hamilton
Piezometer	77-6-2	ML-06-2	G-5	84-2-1	OW15-2	UW28-2
Date	11/1/82	16/9/85	3/5/85	20/8/85	7/16/82	11/11/83
Chloride (mg/l)	103	1040	202	550	560	4360
TOC (mg/l)	43	6490	145	294	17	4600
Volatile Halocarbons (ug/l)						
Chloroform	<0.1	3.0	<MDL	<MDL	<MDL	1.5
1,1,1-Trichloroethane	<MDL	0.1	0.14	0.1	2.8	0.1
Carbon Tetrachloride	0.1	<MDL	<MDL	8.0	<MDL	<MDL
Trichloroethyelene	0.29	21	<MDL	<MDL	0.6	<MDL
Tetrachlorethylene	<MDL	<MDL	<MDL	0.1	0.02	<MDL
Volatile Aromatics (ug/l)						
Benzene	3	9.1	45	8.5	n.r.	27
Toluene	<0.2	320	2.4	730	n.r.	242
Ethylbenzene	<0.2	12	58	13	n.r.	74
Chlorobenzene	<0.2	3	10	<MDL	n.r.	<MDL
m-plus p-xylene	<0.2	28	94	27	n.r.	191
O-xylene	<0.2	22	12	40	n.r.	123
1,2,4-Trimethylbenzene	<0.2	<MDL	53	14	n.r.	51
Napthalene	<0.2	19	21	63	n.r.	60

MDL - less than the method detection limit.
n.r.- not reported.

This paper describes some of the current studies at the six landfill sites. It is impractical to examine the distribution of the forty to one hundred organics commonly identified in landfill leachate, especially considering the need to analyze groundwaters from thirty to one hundred points to adequately define their spatial distributions. Therefore, at each site a detailed characterization of landfill leachate was conducted and specific organics were selected for more detailed study. To date, these studies have emphasized commonly encountered, more mobile organics which can routinely and reliably be determined in numbers sufficient to provide accurate "snapshots" of their distribution in groundwaters. These distributions are then interpreted in terms of the hydrogeological processes (advection, dispersion) and geochemical processes (sorption, chemical and microbial reaction) which must control the distributions. These well-characterized sites will be used in the future to examine the migration of less-mobile organics of particular environmental concern.

In the context of the above rationale, landfill studies to date have emphasized two classes of volatile organic contaminants:

1) halogenated, one-and-two carbon hydrocarbons which are common industrial chemicals that regularly occur in household products, and
2) aromatic hydrocarbons, occasionally chlorinated, that are common in petroleum products and other industrial chemicals as well as in household products.

The specific organics considered are listed in Table 1. Other organics commonly encountered in landfill leachate plumes are discussed by Reinhard et al. (1984). This paper will emphasize the mobility and persistence of these organics relative to indicator parameters, such as chloride (Cl^-) and non-volatile, dissolved or colloidal organic carbon (TOC), which are considered to migrate at the same velocity as the groundwater and, in the case of Cl^-, are not sorbed nor transformed.

BORDEN

Studies of the hydrogeology and inorganic geochemistry of the leachate plume from the CFB Borden abandoned landfill culminated in the special issue of the Journal of Hydrology (vol. 63 no. 1/2, 1983). Selected piezometers were sampled for organic contaminants. Results pertinent to this study are summarized in Table 1 and the total volatile halocarbon concentrations are shown in Figure 1.

The plume is migrating in an unconfined aquifer in stratified sands. The chloride plume, shown in cross-section in Figure 1, shows some effect of input concentration fluctuation, but clearly indicates the dilution in the flow direction attributed to dispersion.

The concentration of volatile organic contaminants in these groundwaters is very low (Table 1) and, if well P-3 is considered background, hardly above background levels. At this landfill most of the refuse was burned during operations from 1940 to 1973 before normal landfilling operations were employed from 1973 to 1976 when site was abandoned. The lack of volatile organics is attributed to this operation history, while possible biotransformations under the methanogenic conditions within the site and hydrodynamic dispersion are probably of secondary importance.

WOOLWICH

The trace organics found in groundwater at the Woolwich landfill site near Waterloo have been discussed by Reinhard et al. (1984) and selected data from a highly-impacted groundwater are presented in Table 1. Although established on sand deposits, landfilling has been conducted in large trenches, seven to ten meters above the water table, since the mid-1960s. In detail, the contaminant distribution, even near the landfill, is complex and irregular, with the upper part of the water table aquifer highly contaminated near the site and the contaminated zone becoming more erratic and deeper in the

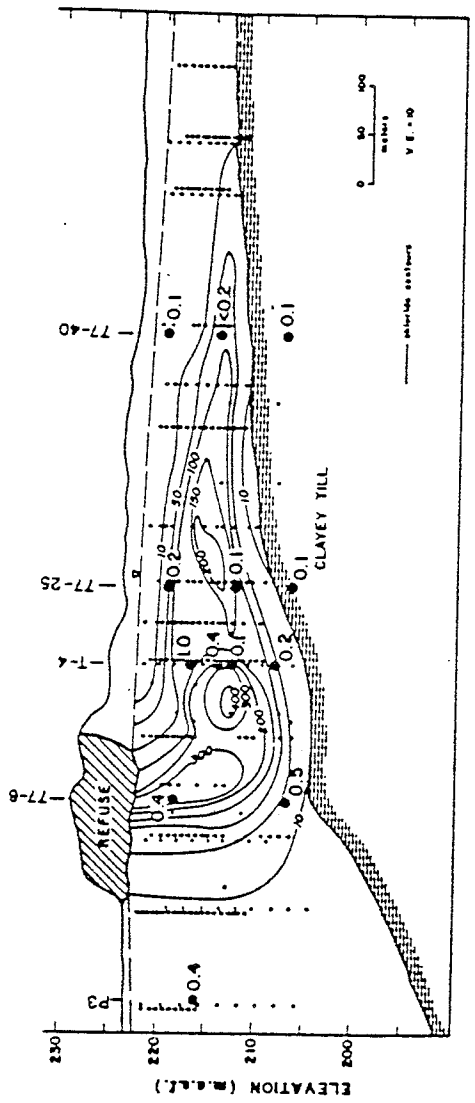

Figure 1. Cross-section through the abandoned Borden landfill showing the distribution of chloride (contoured) and the total volatile halocarbons, January, 1982.

aquifer to the south and southeast of the site. Figure 2 uses the maximum chloride value at each multilevel piezometer to define the lateral extent of the plume in 1984. In its three-dimensions, the plume is less regular than Figure 2 indicates.

Zapico (M.Sc. thesis, in progress) developed a coring technique to obtain representative cores of the aquifer. Detailed profiling of hydraulic conductivity over five to ten centimeter lengths of core is underway, as is an evaluation of borehole and piezometer hydraulic testing in order to provide an improved definition of the site hydrogeology—a basic requirement for the interpretation of organic contaminant distributions. Initial assessment of hydraulic conductivity and gradients (water-table configuration) suggests that conservative leachate tracers, such as Cl^- should be moving fifty to two hundred and fifty meters laterally each year. Given the twenty year landfilling history, the chloride plume should extend beyond the limits of Figure 2,

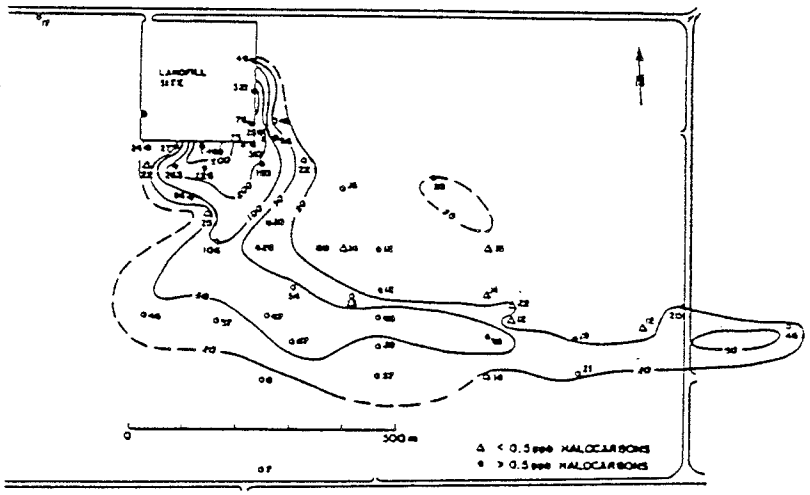

Figure 2. Plan view of the landfill-leachate plume at the Woolwich site. The maximum chloride concentration at each multilevel is contoured and occurrences of significant volatile halocarbons indicated.

whereas the plume becomes poorly defined after five hundred meters. Either the hydraulics are incorrectly perceived or the dilution by dispersion is sufficient to obscure the plume front. The multilevel piezometers where more than 0.5ppb total volatile halocarbons were detected in any of the samplings from 1982 to 1984 are circled in Figure 2. The occurrence of these organics and possibly elevated Cl^- levels suggests that very diluted leachate has migrated more than one kilometer from this site. The distal segment of the plume is being monitored for evidence of increasing Cl^- and trace organic levels that would support the assertion that contaminants should have reached this distance in significant concentration.

In terms of the volatile halocarbons and aromatics listed in Table 1, the Woolwich plume has a slightly different mix of contaminants compared to the other sand aquifer plumes. Trichloroethylene dominates the halocarbons and 1, 2, 4-trimethylbenzene is in lower concentration. This could relate to landfill composition, the presence of a thick unsaturated zone only at this site, or to unique geochemical processes active at this site. Such speculations may be better addressed when the hydrogeology is better understood.

NORTH BAY

The most intensively studied landfill site is at North Bay, Ontario (Reinhard et al., 1984; Barker et al., in press). The landfill lies in a complex deposit of bedded glaciofluvial sands underlain by gneissic bedrock. The site has operated since 1962 and leachate-contaminated groundwater has been observed discharging near a creek, about eight hundred meters from the landfill, since our studies began in 1980 (see Figures 3 and 4). Thus, at this site we have not been able to discuss a plume front, as is found at the other sites. Mobile contaminants have reached the discharge zone, albeit at very low concentrations. This study, therefore, cannot deal with relative velocities of contaminants, but rather provides field evidence of contaminant transformation and persistence during transport in anoxic groundwater.

The organic geochemistry of the leachate is presented by Reinhard et al. (1984) and Barker et al. (in press). Table 1 presents an analysis of a highly impacted groundwater pertinent to this discussion. Volatile halocarbons do not persist throughout this plume, probably due to their biotransformation

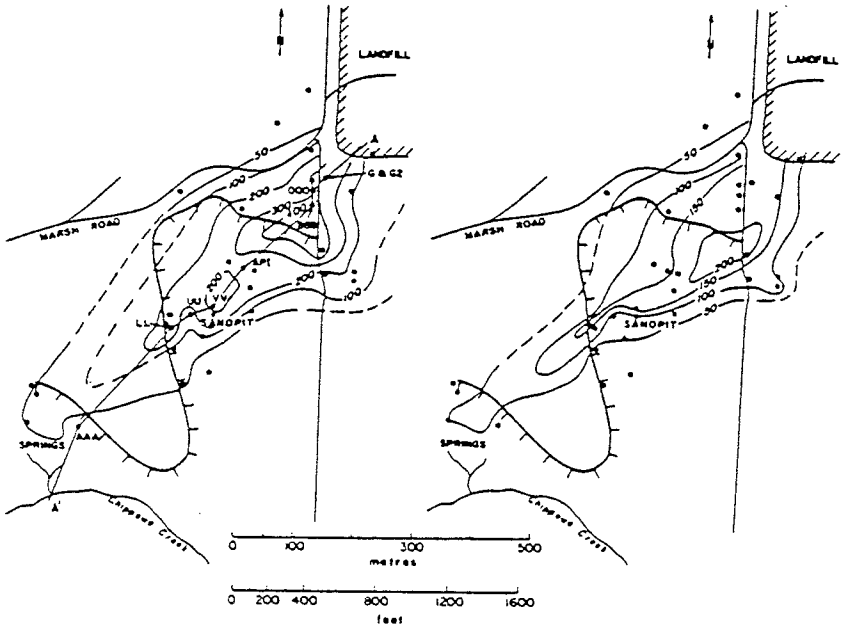

Figure 3. Plan view of the North Bay leachate plume showing the distribution of the maximum chloride (left) and TOC (right) concentrations Data from 1984.

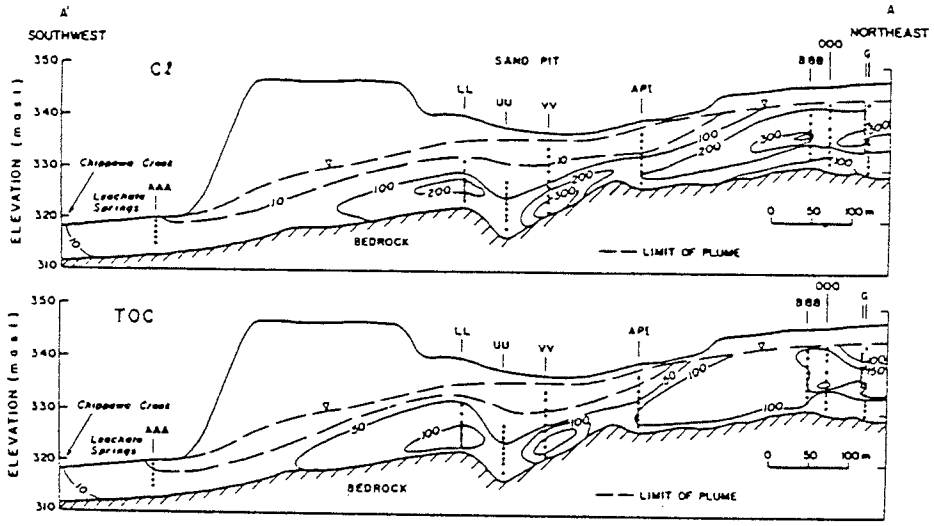

Figure 4. Distribution of chloride and TOC in groundwater samples along cross-section AA' (see Figure 3). Data from 1984.

under the methanogenic conditions of this plume. Volatile aromatics are more persistent, however, and are found in the discharge zone, although at significant attenuation.

Recent hydrogeological studies (M. Moore and N. Gensky, M.Sc. theses in progress) have identified a surprisingly uniform stratigraphy in the subsurface (see Figure 5) which contrasts sharply with the complex fluvial sands apparent above the water table. A relatively thick sand of rather uniform appearance and hydraulic conductivity (about $1x10^{-2}$ cm/s) may extend throughout the flow system. Average groundwater velocities appear to be from $4x10^{-4}$ cm/s to $1x10^{-3}$ cm/s. Unretarded contaminants could, therefore, be moving through the flow system withing two to four years. This is more than twice the velocity calculated from earlier, less extensive studies.

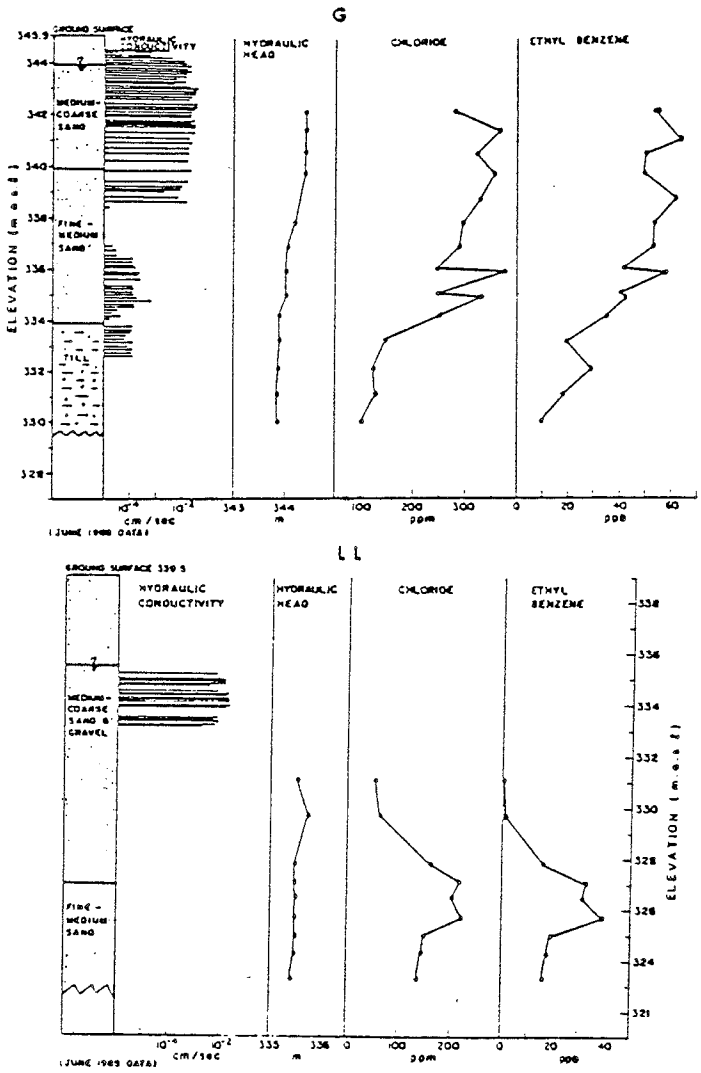

Figure 5. Vertical variation of selected hydraulic and geochemical parameters at locations G and LL (see Figure 3) in the North Bay leachate plume.

Spatial and temporal variability of contaminant distributions have been the focus of recent studies. Figure 5 indicates vertical variability in hydraulic characteristics and selected contaminant distributions at piezometer G, adjacent to the landfill, and at piezometer LL, about five hundred meters down-gradient. Vertically, the chloride and ethylbenzene co-vary, with the highest concentrations found in the fine-medium sand, the unit which conducts the major flux of leachate. Figure 6 demonstrates the temporal variability (May to September, 1985) of contaminant and leachate-indicators chloride and total organic carbon (TOC) at single sampling points from each site (LL-9, G-5). Data collection is continuing and will be combined with data from 1982 onwards in a rigorous evaluation of temporal variability and its causes. The dominant source of temporal variability is probably the variation of contaminant inputs from the landfill, although selective biotransformation and hydraulic flow changes could also be significant causes. Given the input variability as the source for variability at G-5, located beside the landfill, it was anticipated that the process of dispersion would bring about more even contaminant distributions over time at piezometer LL. Dispersion is considered a major agent for the generation of the attenuated but

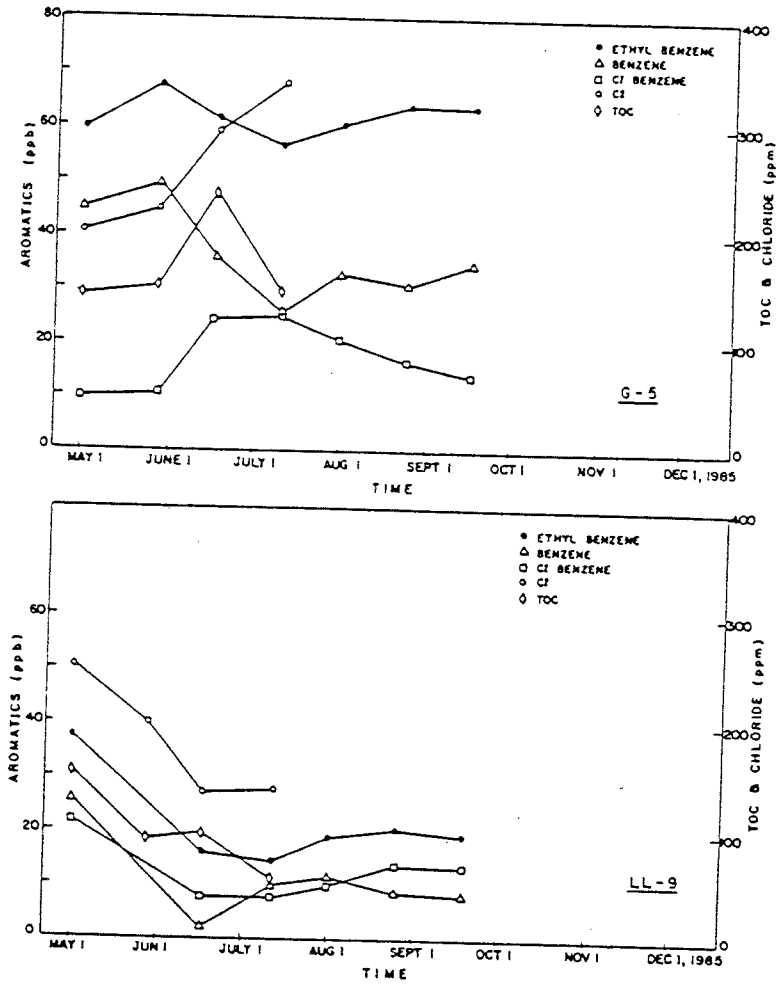

Figure 6. Temporal variability of groundwater quality at piezometers G-5 and LL-9, North Bay leachate plume.

"smoothed" contaminant distributions of the Borden plume (MacFarlane et al. 1983). At Borden, the major source of dispersion is likely the small-scale (10 cm to 2 m) hydraulic heterogeneities of the sands. Although there is excellent geophysical evidence for small-scale layering at North Bay, the hydraulic conductivity distributions, indicated in Figure 5, appear much more homogeneous than at Borden. This suggests that dispersion may be less significant in the North Bay plume and may account for the persistence of temporally-variable contaminant distributions along the plume.

The apparently variable contaminant input to the flow system and this persistent variability in the plume at North Bay precludes direct, simple evaluation of contaminant distributions to assess chemical or biological processes that may remove certain contaminants. Barker et al. (in press) considered the fate of selected organics that co-vary at the start of the plume (piezometer G), probably reflecting a covariance in their input to the system. By examining the distribution of covariant pairs of organics at piezometers along the eight-hundred-plus meter plume, the relative persistences were evaluated. All xylene isomers appeared to be biotransformed more rapidly than ethylbenzene, while 1, 2, 4-trimethylbenzene is being removed faster than 1, 4-dichlorobenzene. These observations are not consistent with the general expectation of non-biodegradability of substituted benzenes under the anoxic conditions of this plume (Wilson and MacNabb, 1983), but the persistence of the dichlorinated benzene, relative to the trimethylbenzene, is perhaps consistent with the enhanced persistence of chlorinated benzenes, relative to the methyl-substituted benzenes (Kuhn et al. 1985, for example). Kuhn and co-workers also report the biotransformation of xylenes under anaerobic conditions.

NEW BORDEN

The new landfill at CFB Borden consists of a series of excavated cells about one hundred and fifty meters by sixty meters, which, starting in 1976, have been filled with municipal refuse and covered. Two cells have been completed and the third is partially full. These cells are excavated into a sequence of fine sand, silty sand till and clayey silt till (Figure 7).

Hydraulic conductivities are in the range of 10^{-3} to 10^{-6} cm/s for the silty sand till with a representative average of 5×10^{-5} cm/s, so contaminant migration should be limited at this nine year old site to shallow depths within 150 to 200 meters of the cells.

Carey (1985) details the hydrostratigraphy and northward-extending plume pattern as defined by chloride (Cl^-) and aqueous, non-volatile organic carbon (TOC). Monitoring on three occasions in 1985 emphasized the Cl^-, TOC, and volatile aromatic contaminants. Table 1 presents some pertinent results for leachate at this site. A south to north cross-section through the oldest cell is presented in Figure 7, indicating the distribution of chloride and two volatile organics, toluene (C_7H_8) and carbon tetrachloride (CCl_4). These plumes are contoured using the chloride plume for 1984 obtained by Carey (1985) as a model although the organic contaminant occurrences are somewhat erratic. For example, upgradient (south) from the landfill, significant chloroform was found in piezometers at M14, while chloride and toluene levels were very low—perhaps at background levels.

This erratic, trace organic distribution makes the discussion of organic mobility relative to the conservative tracer Cl^- difficult. Chloride and carbon tetrachloride have both reached M18 at somewhat reduced concentrations. Toluene has reach B84-13 and may also have reach M17. This would indicate carbon tetrachloride is as mobile as chloride, while toluene is slightly less mobile. Since these organics are slightly hydrophobic, but of similar hydrophobicity (for example, their octanol-water partition coefficients are both about four hundred to six hundred), they both would be expected to be retarded somewhat with respect to chloride (Karickhoff, 1984). The fact that this expectation is not apparently met could be due to a number of factors, including 1) a low sorption potential of the porous media, 2) spatial and temporal variability in their inputs to the flow system from the landfill, and 3) biotransformation of toluene causing its greater apparent retardation. A

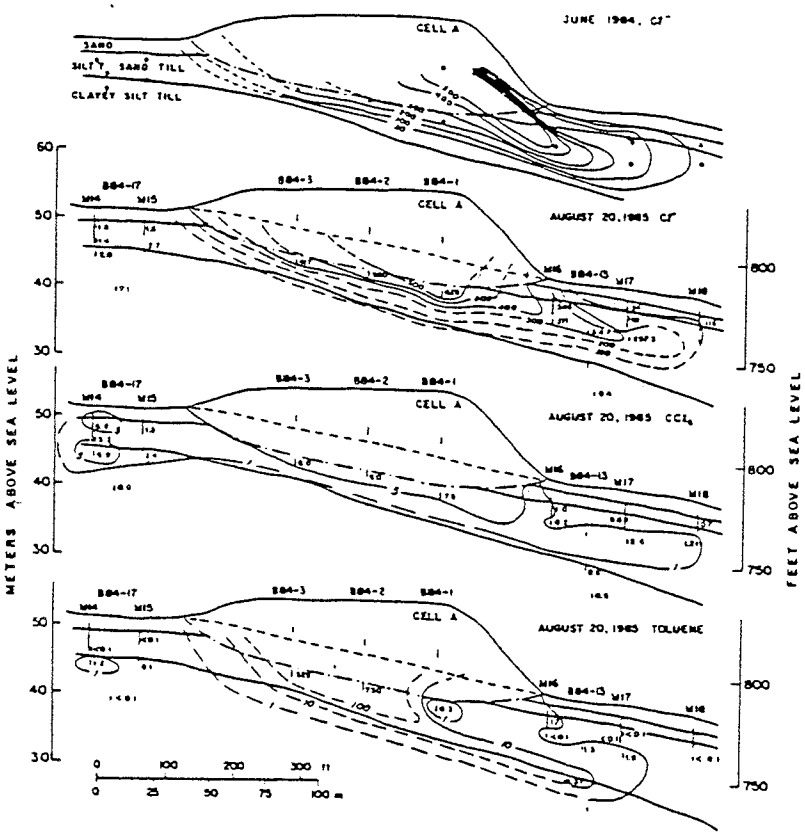

Figure 7. Cross-sections through the oldest landfilled cell at the New Borden site showing the distribution of chloride in 1984 and August 1985; carbon tetrachloride, August 1985; and toluene, August, 1985.

more comprehensive view of contaminant distributions is clearly required and current studies at this site should provide a clearer description of contaminant migration.

BAYVIEW

The Bayview Park landfill in Burlington is an 18 hectare site which operated from 1961 to 1974. It is located just under the Niagara Escarpment (schematically shown in Figure 8). Largely municipal waste was landfilled in shale quarry excavations in the Queenston Formation. The red silty mudstone with occasional dark-grey-green seams extends to a depth of one hundred and thirty-five meters and is highly fractured. Fractures are mostly sub-horizontal bedding plane fractures which impart most of the permeability to this rather impermeable unit. Hydraulic conductivity ranges from 10^{-4} to 10^{-10} cm/s (Hewetson, 1985).

Groundwater samples were obtained from conventional piezometers and multilevel devices (Cherry and Johnson, 1982). Samples of the analysis of leachate indicator paramters (dissolved organic carbon, organic nitrogen and phenol was by standard techniques, but a unique syringe-and-sorption cartridge sampling system (Pankow et al., 1984) was used for trace organics. Although a wide-range of organics was found in groundwaters, including alkanes, benzene, toluene, xylenes, and sulphur-bearing heterocyclics, studies

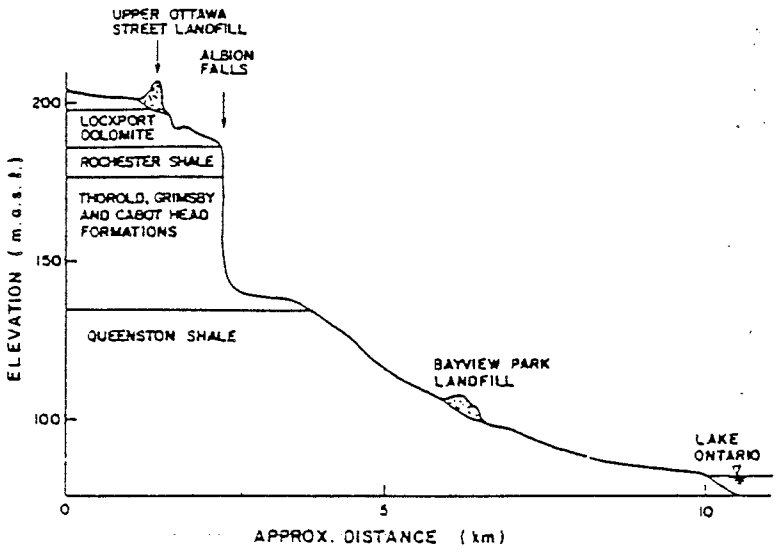

Figure 8. Schematic locations of the Bayview Park (Burlington) and Upper Ottawa Street (Hamilton) landfill sites indicating the general contaminated groundwater flow paths envisaged.

concentrated upon three xenobiotics -1,1,1-trichloroethane, chlorobenzene, and 1,4-dichlorobenzene (Pankow et al., 1984). Representative results for a highly-impacted groundwater are shown in Table 1. Although small amounts of these materials could have originated with the piezometer materials, the major source was likely the landfill (Hewetson, 1985).

The distribution of these three organics in groundwater is rather erratic. Given the complexity of hydraulic flow in fractured systems, this is not unexpected. Hewetson (1985, Figure 17) presents the distribution of 1,1,1-trichloroethane in a cross-section parallel to the regional groundwater flow towards Lake Ontario. Near the landfill, values of 1 to 19 ug/l are found. A multilevel piezometer about five hundred meters down gradient had 9 and 28 ug/l 1,1,1-TCEa, while conventional piezometers about 850 meters downgradient indicated only 0.5 and 0.2 ug/l 1,1,1-TCEa. A shallow distribution of contaminants is likely.

Water infiltrating the landfill since its opening would still contain measurable tritium. Most of the groundwaters containing the trace halocarbons also contain measurable tritium, supporting a landfill source, of trace organics. However, a significant number of groundwaters, essentially free of tritium, contain 1,1,1-trichloroethane. This may reflect leaching from multilevel piezometer packer material in a few cases but not generally. Hewetson (1985) proposes that contaminant transport is advective in fractures with diffusion occurring into the non-fracture-connected porosity of the mudstone. Since some organic solutes diffuse more slowly than tritium or Cl^-, one would expect that water migrating in the fracture would lose tritium more rapidly than trace organics due to diffusion into the matrix. This process could account for some occurrences of 1,1,1-trichloroethane in tritium-free groundwaters. This advection-diffusion transport concept was suggested by Gillham et al. (1984) to be applicable to layered porous media as well, although Sutton and Barker (1985) did not find supporting evidence in a natural gradient field injection experiment involving organic solutes and chloride.

Other factors could also contribute to the erratic distribution of trace

organics, including variable inputs from the landfill or elsewhere, selective organic biotransformation and complex, discrete fracture flow paths with poor interconnections.

HAMILTON

The Hamilton site - specifically the Upper Ottawa Street landfill - is located within 750 meters of the Niagara Escarpment near Red Hill Creek. Its geological position is shown schematically in Figure 8. The 18 hectare site received municipal and industrial waste from the mid-1950's until 1978. Industrial waste included large volumes of liquids. Some waste was burned during disposal. Landfilling occurred in an abandoned limestone quarry where a thin clay till was removed, providing easy access of leachate to the fractured carbonate-shale bedrock. The regional groundwater flow is southeastward towards the Escarpment. Mounding of the water table into the landfill could also cause water to move outwards in any direction, but migration of hundreds of meters distances is only likely within the regional flow system.

The site is underlain by cherty, shaley dolomite of the Lockport Formation which is underlain at a depth of about 5 to 10 m by shale of the Rochester Formation which is 7 to 10 m thick. The dolomite is fractured with most being well-connected, sub-horizontal bedding plane fractures, but some sub-vertical fractures do contribute to a moderate hydraulic conductivity of about 10^{-2} to 10^{-3} cm/s. The underlying shale is less permeable generally, with hydraulic conductivity typically 10^{-6} to 10^{-9} cm/s. Locally, however, major horizontal and vertical fracture permeability does exist. The general flow path is discussed by Cherry et al. (1984). Shallow, lateral flow towards the Escarpment dominates in the dolomite with vertical movement in the shale being most prominent near the Escarpment where relaxation of horizontal stress probably causes more vertical permeability. As with all fractured systems, some alternate discrete flow paths could exist.

The pertinent chemistry of leachate at the landfill is listed in Table 1. Groundwater samples were obtained from multilevel piezometers described by Cherry and Johnson (1982). Sampling and quality assurance information and detailed results is presented by Cherry et al. (1984) and a more detailed discussion of results is in preparation. Studies of some solid material in the site and of leachate indicates that most of the identified organics are hydrocarbons such as aliphatics, aromatics, polycyclic aromatics and heterocyclic compounds (Cherry et al., 1984). C_4 to C_{20} carboxylic acids and aromatic acids, typical of landfill leachate, are prominent. Given the industrial disposal at this site, the lack of halogenated organics, either in the adjacent groundwaters, leachate or landfill solids, is pleasantly surprising. Unfortunately, such volatile halocarbons would have been excellent "tracers" of landfill leachate and their general absence complicated the identification of leachate migration.

Cherry et al. (1984) recognized two types or end-members for uncontaminated background groundwaters. One is a recently-recharged, tritium-containing, low-inorganic-load water; the other is a much older, tritium-free, high-inorganic-load water, similar to background water found in the Queenston shale near the Bayview site and commonly occurring in this carbonate-shale bedrock. It could represent, in part at least, formation brines or could be formed by meteoric water being in contact for long periods of time with relatively-soluble carbonate, shale and evaporite beds. Without the presence of leachate-derived, mobile xenobiotics such as volatile halocarbons and the often poor background water quality, no good indicator of leachate was available. One of the best second choices was the volatile aromatics which were present in leachate at 10 to 300 ug/l levels, but which are naturally - occurring compounds found in poor-quality, uncontaminated groundwaters at less then 10 ug/l levels.

The distribution of one such aromatic, toluene, is shown in Figure 9. The concentrations are shown beside the appropriate sampled piezometer. Each sampling port was located, if possible, in fracture zones, judged from examination of continuous core in each borehole, but at irregular depths down to about 45 meters. Figure 9, then, provides only an approximate rep-

resentation of vertical distributions. Most toluene concentrations above 1 ug/l are observed in shallow groundwaters within one hundred meters of the site or downgradient, to the east-southeast.

In order to define groundwaters impacted by landfill leachate, fourteen parameters and combinations of parameters were evaluated (Cherry et al. 1984). These included concentrations of inorganics, organics and ratios of inorganics. Each groundwater was then ranked as having a strong, a weak,

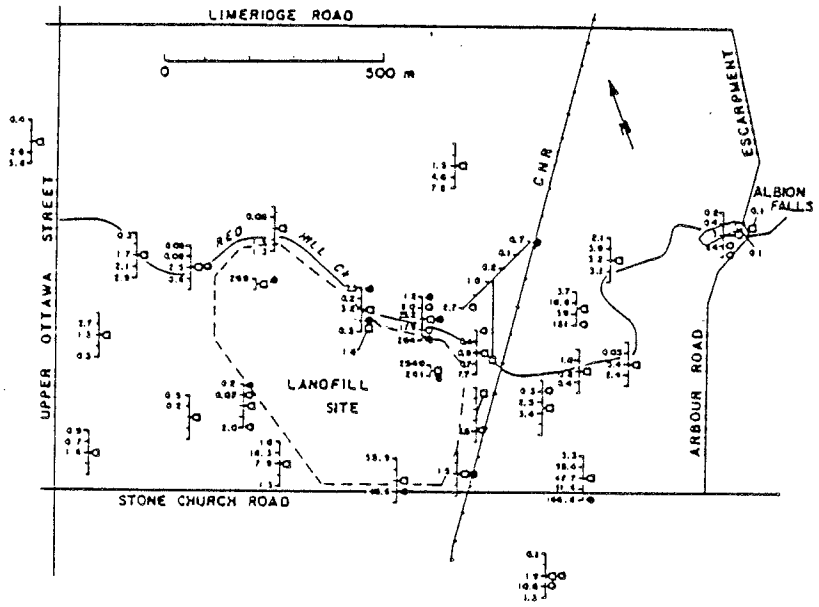

Figure 9. The distribution of toluene concentrations (ug/l) and strong (solid dots) and weak (open dots) leachate impacts in groundwater at the Hamilton site.

or an insignificant indication of leachate impact. These results are indicated in Figure 9 as solid dots, open dots, or no dots, respectively. Piezometer points from which representative samples could not be collected have neither a toluene concentration, nor a dot.

The distribution of leachate-impacted groundwaters is rather irregular. Most impacted samples were obtained from shallow fracture-zones in the Lockport Formation. The occasional indications of leachate within and below the Rochester shale may represent some vertical penetration of leachate or may represent some combination of very poor background water quality coupled with some leaching of organics from the PVC piezometer material and organic packer. The relatively minor leachate impacted apparent at this site was unexpected, given the reported disposal of liquid industrial waste. If, as Cherry et al. (1984) indicates, this is the case, the responsible processes are of great interest. It is not possible to identify the attenuating processes, but they could include the burning of liquid waste, the lack of hazardous organics in the original waste, biotransformations within the landfill or the plume, very significant dispersive dilution, and sorption onto or diffusion into the rock matrix.

If the background water was of better quality, it may have have been possible to identify a greater extent of leachate impact. On the other hand, some minor leachate impact has been attributed to groundwaters containing trace levels of organics such as aromatic hydrocarbons and heterocyclics which may, in fact, be naturally-occurring in these rocks. Research is underway to provide a clearer picture of natural occurrences of such compounds.

COMPARISONS, GENERALIZATIONS, AND CONCLUSIONS

Volatile halocarbons and aromatic hydrocarbons are ubiquitous in leachate produced from landfilled, normal municipal refuse. However, where refuse has been burned (Borden) much lower concentrations are found. The concentration of particular organics in leachates varies widely from landfill to landfill, probably reflecting the specific hydrogeological and microbial/ geochemical conditions within the landfill as well as the particular materials landfilled. Where toxic wastes or industrial wastes are co-disposed with municipal refuse, much higher concentrations of these organics may be found in some contaminated groundwaters (Jackson et al., 1985, for example), but may be less-common in others (the Hamilton site, for example).

Where landfill leachate impacts shallow, unconfined sand aquifers these organics appear to have migrated about as far as non-reactive, conservative tracers such as chloride. This indicates that sorptive retardation is minimal in sand aquifers such as Woolwich and North Bay, probably reflecting the dearth of solid organic matter, the major sorbant for organics, in such aquifers. Even in the sand till of the new Borden site, where organic matter may be more abundant, carbon tetrachloride appears to have migrated as far as chloride although the aromatic hydrocarbon toluene does not appear to have travelled as far. This apparent attenuation of toluene could reflect greater sorptive retardation, more biodegradation, or a different input history for the aromatics relative to chloride and carbon tetrachloride. Although the picture is far less clear in the fractured shale/carbonate flow system, there is no evidence of significant retardation of these organics relative to chloride.

In all contaminated aquifers, the attenuation of organic contaminants along the flow system has been dramatic. High organic concentrations near the landfill give way to much lower concentrations within one hundred to five hundred meters. This attenuation is due primarily to dilution by dispersion, but biodegradation contributes in the case of some organics. For example, the decrease in volatile halocarbons and certain volatile aromatics at the North Bay site has been attributed to biodegradation under strictly anaerobic conditions (Barker et al., in press). It is likely that anaerobic transformations occur in almost all landfills and their leachate plumes, but it is not possible at this time to confidently predict the resultant attenuation of organic contaminants.

Temporal variability of contaminant concentrations in landfill leachate plumes is significant. The major contribution is probably the temporal variability of contaminant input from the landfill. Dispersion should dampen temporal variability, but at North Bay in particular, temporal variability persists through the flow system. The problem of temporal variability must be addressed in order to establish a scientific basis for designing groundwater monitoring programs.

The distribution of organic contaminants in groundwaters at the landfill sites situated on fractured rock is much more erratic than in impacted groundwaters in sand aquifers. This might be attributed to migration in discrete fractures as opposed to migration in granular porous materials. Monitoring in fractured flow systems would appear to be much more difficult, since the discrete fractures carrying leachate may be difficult to intersect.

ACKNOWLEDGEMENTS

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by A-CUBED, Mississasuga. The studies at the Hamilton site were conducted for the Upper Ottawa Street landfill site committee with support from the Ontario Ministry of Health. Much of this research was conducted in cooperation with Dr. J. Cherry and numerous staff and graduate students within IGR, whose assistance and advice is gratefully acknowledged.

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J-12

DIFFUSIVE CONTAMINANT TRANSPORT IN NATURAL CLAY: A FIELD EXAMPLE AND IMPLICATIONS FOR CLAY-LINED WASTE DISPOSAL SITES

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ABSTRACT

Vertical core samples were obtained from holes drilled into an impervious, unweathered water-saturated clay deposit beneath a five-year old hazardous waste disposal cell at a site in southwestern Ontario. After sectioning the cores, pore water obtained by squeezing numerous core segments was analyzed for chloride and volatile organic compounds. Waste-derived chloride was detected in the clay to a maximum depth of 83 cm below the bottom of the cell. The most mobile organic compounds were found only to a depth of ~15 cm. Although a distinct downward hydraulic gradient existed in the clay because of the high water table in the waste, the vertical chemical profiles in the clay were the result of molecular diffusion. The smaller distances of penetration for the organic compounds relative to chloride are attributed primarily to adsorption. Because the clay deposit at the site is 25 m thick, it will take thousands of years for contaminants to diffuse through the clay into the underlying aquifer. This study has implications with respect to low-permeability clay liners used at waste disposal sites. For liners of typical thickness (~1 m) molecular diffusion will cause breakthrough of relatively mobile contaminants in less than 5 years, and the flux of contaminants out of such liners may be significant.

INTRODUCTION

The use of clay liners at waste disposal sites is frequently advocated as a means of minimizing the potential for groundwater contamination. It is commonly thought that if the hydraulic conductivity (K) of the clay is low and if there are no structural defects, then the liner will provide a barrier between the waste and the underlying hydrogeologic domain. Guidelines for the properties of clay liners commonly specify that they should have a K less than 1×10^{-7} cm/s so that the rate of advective transport will be small. Even when advection is minimal, however, contaminants can migrate through the clay at rates that may be significant. This non-advective migration is caused by molecular diffusion.

A field investigation of contaminant migration in a natural clay deposit beneath a completed cell at a hazardous waste disposal site is described here. The clay is unweathered, uniform, and has a very low K ($< 5 \times 10^{-8}$ cm/s). It thus has all of the features normally desired of a clay liner. Contaminant profiles with depth were measured in pore water extracted from core samples of the clay underlying the site. The goals of the investigation were to determine the rates at which inorganic and organic compounds from the waste migrate downward through the clay and to assess the applicability of simple diffusion models for predicting these rates.

SITE SETTING AND PREVIOUS STUDIES

The waste disposal facility, operated by Tricil Limited, is located 15 km southwest of Sarnia, Ontario (Figure 1). The site was selected for this study primarily because the natural clay deposit is 25 m thick and therefore vertical boreholes through the waste could be drilled a meter or two into the

underlying clay without destroying the integrity of the overall deposit. The site possesses additional positive attributes, such as waste material that offers no obstructions to drilling, accurate information on the locations and depths of the cells, and hydrogeological conditions that have been determined in detail in previous investigations. The waste-disposal cell selected for this investigation was excavated in 1979, and received its final load of waste in 1980. The waste mass consisted of flyash from a nearby coal-fired electrical generating station to which the liquid hazardous wastes were mixed prior to disposal. The cell is approximately 15 m deep, with a 2 m thick cover of compacted clay.

The study site is situated in the St. Clair clay plain, which extends more than 20 km in all directions from the site (Figure 1). The clay deposit which is late Quaternary in age, was formed by glaciers that protruded into a large glacial lake. The deposit contains numerous granules of shale bedrock indicative of the glacial-till origin of the deposit. About 40% of this glacial till is clay-sized particles, which are primarily illite and chlorite (Quigley and Ogunbadejo, 1). The remainder consists of silt and sand-sized material and a small percent of pebbles.

Desaulniers (2), and Desaulniers et al. (3,4) have studied the permeability of the clay, and the flow rates and age of groundwater in the clay at several locations on the clay plain including the site described here. These investigators concluded that, below about 5 m from ground surface, the clay is unweathered, and has an average K less than 5×10^{-8} cm/s. Groundwater flow is downward at an average linear velocity less than several millimeters per year. Isotopic dating studies of the groundwater in the unweathered clay indicated that it is generally many thousands of years old. Desaulniers and co-workers also concluded that natural solutes in the

groundwater, such as Cl^- and ^{18}O have developed vertical concentration profiles up from the underlying bedrock due largely to molecular diffusion since the retreat of the Pleistocene glaciers. Desaulniers et al. (4) successfully simulated the vertical concentration profiles by means of one-dimensional diffusion models and diffusion times of 12,000 to 16,000 years.

Goodall and Quigley (5) and Crooks and Quigley (6) determined vertical profiles of several inorganic, leachate-derived constituents by the analysis of core samples taken from weathered clay at the bottom of shallow pits at a nearby municipal landfill in Sarnia. While the data suggested diffusion as the dominant cause of profile development, they only had limited success in the fitting of a diffusion model to the data. This was in part due to advective transport in fractures in the weathered zone. The current investigation has some similarities to the work of Quigley and co-workers, but differs in that it examines the clay at greater depth where it is unweathered, and in that it includes organic contaminants.

EXPERIMENTAL

Sample Collection and Preparation

Samples from three boreholes located approximately 5 m apart in one 5-year old cell were collected using a Central Mine Equipment (CME Model 75) drill rig with continuous flight, 1.6 m (5 foot) long hollow-stem augers. Beginning approximately 0.5 m above the bottom of the cell, cores were taken with a 1.6 m (5 foot) split spoon tube sampler. In this manner, samples were collected from the bottom of the flyash and into the underlying clay to a depth of approximately 2 m below the interface. As the samples were brought to the surface, they were removed from the split-spoon sampler and lightly

washed with water to remove most of the external contamination.

Immediately after sampling, the cores were taken to an on-site laboratory and placed in a fume hood for further sample preparation. The interface between the flyash and clay was easily located because of its abruptness. Moving both directions from the interface the core was cut into either 3.8 or 7.6 cm (1.5 or 3 inch) sections with a sharp knife. The contamination on the exterior of each section was then carefully cut away with two frequently-cleaned knives. Each section was wrapped in aluminum foil which had previously been heated at 450°C for one hour. Each core section was then placed in a 500 mL amber jar whose cap was lined with aluminum foil. Both the jar and the foil had been heated at 450°C. The samples were then stored at 4°C.

Pore water was removed from the core sections by compressing the sections in specially designed consolidometers (Figure 2). These devices, which were similar in design to those described by Patterson et al. (7), were capped cylinders which contained a moveable piston. Pressure was exerted on the sample by the piston, which was driven by compressed nitrogen. Samples were typically pressed to 600 psi (42 kg/cm^2). The piston area was 44 cm^2, thus a total force of approximately 2000 kg was exerted on the sample. In the bottom of each consolidometer were a series of glass-fiber filters (Gelman Inc., Ann Arbor, MI) and screens (100 mesh stainless steel) and a 1/16 inch o.d. tube which carried the pore water to a 10 mL syringe. The syringe was fitted with a small teflon valve (Mininert, Pierce Chemical, Rockford, IL) to facilitate removal of the syringe from the consolidometer. In order to minimize both volatilization from the syringe and the pressure within the syringe, the plunger was replaced with a teflon cap which was machined to fit inside the barrel of the syringe. The cap floated on top of the liquid as the

syringe filled (surface tension prevented the water from creeping around the cap). At the completion of squeezing, the valve on the syringe was closed, and the syringe was removed. A teflon-tipped plunger was placed into the top of the syringe, the valve opened, and the liquid transferred to two sample bottles. The first bottle (1.5 mL pre-cleaned amber glass) was carefully filled to minimize volatilization; no significant headspace remained. This bottle was capped with a teflon lined septum and stored for organics analysis. The remainder of the sample was then placed in a 25 mL amber glass bottle and saved for inorganics analysis. Both sample bottles were stored at 4°C until analyzed. Pore-water extraction was carried out at 10°C to ensure that concentrations in the extracted pore water were the same as in the undisturbed clay.

The portions of the consolidometer which came into contact with the sample were made of 304 stainless, glass or teflon. A set of 9 consolidometers was used. Between uses the consolidometers were disassembled, washed with soap and water and acetone and heated for at least 6 hours at 250°C.

Chloride Analysis

Chloride analyses were performed using ion chromatography. In addition to the regular sample analyses, approximately 15% of the samples were resubmitted as blind duplicates. Synthetic samples, spiked samples and serially diluted samples were also submitted for quality assurance. Accuracy and precision were excellent on all samples. Extracts from one core (No. 1) were analyzed for major cations and trace metals and those results will be reported elsewhere.

Organics and Total Organic Carbon (TOC) Analysis

Volatile organic compound analyses were carried out by purge and trap with whole column cyrotrapping (P&T/WCC) on a gas chromatograph/mass spectrometer/data system (GC/MS/DS) as described by Pankow and Rosen(8). Briefly, an aliquot of a sample was first diluted with organic-free water to 5.0 mL in the purge vessel of the P&T unit. The volume of the aliquot varied between 0.030 mL and 1.0 mL, and depended on the expected concentration. The aliquot size was 1.0 mL for samples relatively far away from the interface, and was decreased as the interface was approached. An undiluted 5.0 mL sample could not be run for the low-level samples since 5.0 mL of sample was not available for these determinations. After dilution, 10 uL of a P&T internal standard (IS) solution in methanol was added to the purge vessel. The IS solution contained 7.7 ng/uL each of bromochloromethane, 1-chloro-2-bromopropane, and 1,4-dichlorobutane. Each sample was then analyzed by P&T/WCC using a Chrompack CP-Sil8 CB 1 um film thickness capillary column (Chrompack, Inc., Raritan, NJ). Quantitation was achieved based on the responses of the characteristic ions of the target analyte compounds and the IS compounds. TOC analyses were performed on one core (No. 1) by oxidation by ultra-violet light and infrared detection using a Dohrmann DC-80 analyzer (Envirotech, Corp. Mountain View, CA).

Water Content and Porosity

The water content and porosity of sections of one of the cores (No. 3) were estimated by drying and weighing portions of the core. A known mass of core section was placed into a pre-tared vial and dried at 105°C for 12 hours. The vial and soil were re-weighed and the weight loss attributed to water loss. Water content (WC) was estimated as the mass of water lost (W) divided

by the total mass of the water and soil (W+S). Porosity (n) of the core sections was estimated using 2.7 g cm^{-2} as the soil particle density of the clay.

Soil Organic Carbon Content

The soil organic carbon contents, expressed as a fraction ($0 \leq SOC \leq 1$), were determined for each section of core which contained a significant amount of the target organic compounds. A combustion method was used (Johnson, (9); Johnson et al. (10)). Steps in the analysis procedure included: 1) the samples of the clay were dried at 80°C to constant weight; 2) the samples were acidified with 5% $SnCl_2$ in 3 N HCl and dried at 50°C; 3) a known mass of sample was placed in a pre-cleaned copper combustion boat; 4) a batch of 12 samples and standards were placed in a sample carousel; 5) each sample was dropped into a combustion oven at 700°C; 6) carrier gas (90% He/10% O_2) swept the CO_2 evolved from the sample into a methanator where it was quantitatively converted to methane; and 7) the methane was detected with a flame ionization detector. All samples were analyzed at least in duplicate and the results averaged.

Two methods of calibration were used; combustion of known volumes of standard solutions of organic compounds (e.g. sugars), and analysis of "standard soils". The standard soils spanned a range of SOC contents (0.11-4.0% SOC as carbon), and had been analyzed previously by several laboratories (Hassett, (11)). These soils were prepared and analyzed in the same manner as the samples. Excellent agreement between the two types of standards was obtained.

Batch Sorption Experiments

Sorption experiments were conducted using uncontaminated soil from the site. The soil was dried to constant weight at 80°C. 10 g quantities of soil were then placed in 40 mL vials, to which 25 mL of water, containing the compounds of interest was added. The vials were equilibrated for 24 hours by tumbling end-over-end at 30 revolutions per minute. Water concentrations were analyzed by headspace GC, calibrated using standard solutions.

RESULTS AND DISCUSSION

Chloride concentrations for three cores are presented in Table I. The samples of flyash from just above the clay interface in each core were analyzed and their concentrations taken as the concentrations at the interface. Concentrations in the core sections were normalized to these values and are also reported in Table I. In each of the cores the Cl^- content was high in the flyash and decreased downward in the clay. Background Cl^- values in the clay were approximately a factor of ten lower than the flyash values and were calculated from the average Cl^- concentrations in the core sections at depths greater than the penetration depths of the flyash-derived Cl^-. Background Cl^- in the clay originated in the bedrock shale beneath the clay. The maximum distances from the interface that flyash-derived Cl^- could be distinguished from background were 83 cm in core 1, 75 cm in core 2, and 46 cm in core 3. The profiles with depth for the cores are presented in semi-log format in Figures 3-5.

The Cl^- concentrations for core 1 exhibit a classic diffusion profile (Figure 6). The Cl^- profile from core 2 shows a reversal in concentration gradient in the middle of the profile but follows the diffusion shape in the

lower portion. Core 3 follows the expected diffusion profile in the sections just below the interface, but then drops sharply to lower values. The reversal in core 2 and the differences in depth of penetration of Cl^- in the three cores suggest that the Cl^- concentrations in the flyash at the interface varied in time. Even when spatial and temporal Cl^- variations in the flyash at the bottom of the pit are considered possible, however, the reversal in core 2 is difficult to explain because its position in the core indicates that conditions changed more than a year after the pit was filled and capped.

The shallow Cl^- profile observed in core 3 may have resulted from depth-dependent effective diffusion coefficients due to heterogeneities in the clay. To evaluate this hypothesis, the porosities of the core 3 sections were estimated from the water content data (Table I). They are similar to the values (35 - 40%) reported for the clay by Hydrology Consultants Limited (12). The porosity of the section nearest the interface (i.e. the 0.0-3.8 cm section) was somewhat lower than those farther into the clay. In fact no pore water was recoverable by compression from this section. This may have been the result of compaction or dehydration during the excavation of the cell. The lower porosity of the clay nearest the interface in core 3 would be expected to cause some restriction in the rate of contaminant migration in the clay. This may account in some degree for the fact that Cl^- migrated a smaller distance in this core. Comparisons with the other cores in this context cannot be made because the water contents of the other cores were not determined.

Organics analysis data for the three cores are given in Table II. Also, as with the Cl^- data, the core concentrations were normalized to the concentrations in the flyash just above the interface. Normalized data for

the organics are plotted versus depth in Figures 3-6. The organic compounds were detected a maximum distance of 15 cm below the interface. The dominant organic compounds, such as benzene, toluene, and ethylbenzene, had concentrations of many hundreds to several thousand ug/L in the flyash at the interface. The limits of detection for these compounds in the clay were on the order of 1 ug/L or less. The fact that they were not found, even at very low concentrations, at a distance of greater than ~15 cm indicates that there was a relatively abrupt migration front. Comparison of the maximum migration distance of Cl^- (83 cm) with the maximum distances for the organic compounds indicates that the organics have been retarded relative to Cl^-. As discussed below, batch sorption and SOC values have indicated that sorption played an important role in retardation.

The TOC profile for the core 1 pore water extends significantly deeper than any of the organic compounds identified by the P&T analysis procedure. Additionally, the sum of the concentrations of the target compounds represents less than one percent of the TOC concentrations. The bulk of the TOC is probably made up of water-miscible compounds, including acetone, methyl ethyl- and methyl isobutyl ketone (Nesbitt, (13)). These compounds sorb only slightly and would, therefore, be expected to diffuse 3-20 times faster than the target organics. Figure 6 suggests that this is the case.

SOC analyses indicate that the clay contains 0.7-1.3% by weight as carbon (average = 1.1%, Table II). Batch sorption experiments using trichloroethene, benzene, toluene, and ethylbenzene in the aqueous concentration range 100-25,000 ug/L result in a highly non-linear sorption isotherm. Partition coefficient (K_d) values at low concentrations are significantly higher than the partition coefficient values calculated using the relationship:

$$K_{d,calc} = K_{oc} \times SOC \quad (1)$$

where K_{oc} is the organic carbon partition constant and SOC is the soil organic carbon content (Table III). This "excess sorption" at low concentrations may be due to non-hydrophobic interactions between the organics and the clay (14). This possibility, and its effect on diffusion are currently being investigated and will be reported on elsewhere. The K_d values reported in Table III are those determined in batch tests where the final concentrations in the water were ~1000 ug/L.

The hydraulic conductivity of the clay was measured by Hydrology Consultants (12) using piezometer tests in the field and by permeameter tests of core samples in the laboratory. Values of K were in the range of 10^{-8} to 10^{-9} cm/s, with a geometric mean value of 6×10^{-9} cm/s. The water table in the waste cell was close to the level of the original ground surface (i.e. it is below the cap). The average level of the potentiometric surface in the bedrock just below the clay was about 7 m below ground surface. A 7 m average difference in hydraulic head therefore acted across the 25 m thickness of clay beneath the pit. Using Darcy's law with a porosity (n) = 0.37, a downward velocity of 0.15 cm/year is predicted. Even if the downward hydraulic gradient across the clay existed from the date of burial of the wastes, and if the only process causing downward Cl^- migration was advection, then the penetration distance would be only 0.75 cm. The observed penetration distances for Cl^- in the three cores (83, 75 and 46 cm) indicate that this advection distance is insignificant in comparison to expected and observed diffusion distances. It is concluded, therefore, that advective flow is not a major influence on Cl^- migration. This conclusion is similar to that arrived by Desaulniers et al.(4) in their investigation of bedrock-derived Cl^- and isotopes in the clay in the Sarnia area. A similar conclusion is reached for

advection of the organics at the Tricil site. Even with their retardation due to sorption, diffusion distances for the organics will be much larger than those resulting from advection.

MODELING

The minor role of advection and the relatively homogeneous nature of the clay make it appropriate to simulate the downward migration of Cl^- and the organic compounds by means of diffusion models based on Fick's second law:

$$dC/dt = D_{e,c}\partial^2 C/\partial z^2 \qquad (2)$$

where z is the vertical direction and $D_{e,c}$ is the effective solute diffusion coefficient in the clay.

Materials diffusing into the clay must first diffuse through the flyash to the interface. Assuming that the contaminant concentrations in the flyash are initially uniform, and that the initial concentrations of the contaminants in the clay are zero, a concentration gradient will form in the flyash near the interface. If the effective diffusion coefficient in the flyash ($D_{e,f}$) is greater than $D_{e,c}$, then the concentration at the interface will stabilize at a value determined by the initial concentration in the flyash and the relative values of the two effective diffusion coefficients. Furthermore, if $D_{e,f} > D_{e,c}$, then concentration profiles in the clay, when normalized to the concentration at the interface will be independent of $D_{e,f}$ and only a function of $D_{e,c}$. Since $D_{e,f}$ is almost certainly greater than $D_{e,c}$ (because the flyash is a much less compact and cohesive material than the clay), the solution to eq 2 is (Crank (15)):

$$C/C_o = \text{erfc}\ [(z/D_{e,c}t)^{1/2}] \quad (3)$$

where C_o = the concentration at the interface.

The diffusion profile for Cl^- in core 1 and simulated profiles based on eq 3 are shown in Figure 6. The solid line represents the measured concentrations in the core sections. The dashed lines are model profiles using a time of 1800 days and $D_{e,c}$ values as indicated. The data for Cl^- display a close match between the observed concentrations and the simulated profile for $D_{e,c}$ = 4-6 x 10^{-6} cm^2/s. This range is quite similar to values observed in the laboratory by Desaulniers (2) and by Crooks and Quigley (6). For core 2, a $D_{e,c}$ = 4 x 10^{-6} cm^2/s produces a good match to the lower portions of the observed Cl^- profile. In the portion of core 2 closest to the interface, however, the Cl^- concentrations are much lower than expected, and the profile is fit best with $D_{e,c}$ = 8 x 10^{-7} cm^2/s.

For core 3 the penetration distance for the Cl^- is much smaller than for the other two cores, and the profile cannot be fitted closely by a single simulation. The portion of the profile closest to the interface is best fit by $D_{e,c}$ = 2 x 10^{-6} cm^2/s. The lower portion of the core is best simulated by $D_{e,c}$ = 3 x 10^{-7} cm^2/s. The latter value is much smaller than those determined in the laboratory studies. This suggests that the initial concentration distribution of Cl^- in the flyash may have changed with time. The possible effects of a non-constant interface concentration on the diffusion profiles have been evaluated. Using a constant $D_{e,c}$ = 4 x 10^{-6} cm^2/s, but varying the concentration at the interface in time, an attempt was made to duplicate the observed profiles in cores 2 and 3. This was not successful, and the reasons for the variations from ideal diffusion behavior remain unclear.

$D_{e,c}$ in the soil is less than the free-solution diffusion coefficient (D)

at the corresponding temperature due to the tortuous path which the molecules must follow through the porous media. This relationship is frequently expressed as:

$$D_{e,c} = D * \mathcal{T} \qquad (4)$$

where $\mathcal{T}$ is a correction factor ($0.0<T<1.0$) to account for tortuosity and porosity effects.

Values of $\mathcal{T}$ for the clay can be estimated using eq 3 from the observed $D_{e,c}$ values for Cl^- and the literature value of D at a corresponding temperature (10°C). For D = 1.5 x 10^{-5} cm^2/s (Li and Gregory, (16)), and $D_{e,c}$ = 4-6 x 10^{-6} cm^2/s, T is in the range 0.20-0.33.

The diffusion model can also used to simulate profiles of the organic compounds in the clay (Figure 6). In this case, not only the effects of tortousity and porosity must be taken into account, but also the effects of molecular size and sorption.

The effect of molecular size on the diffusion coefficient can be estimated for the compounds using literature data. For example, D values have been measured for a variety of organics in dilute aqueous solution by Bonoli and Witherspoon (17). They suggest that values of D in the range 5-9 x 10^{-6} cm^2/s are appropriate for benzene, toluene, and several cycloalkanes at 25°C. D values for other compounds can be estimated from their data using an approximation equation for the diffusion coefficient which takes into account the effect of molecular size (Wilke and Chang, (18)):

$$D_1/D_2 = \left| \frac{MW_2/r_2}{MW_1/r_1} \right|^{0.6} \qquad (5)$$

where D_1 and D_2 are the free solution diffusion coefficients of a pair of organic compounds of interest at the temperature of interest, MW_1 and MW_2 are their molecular weights and r_1 and r_2 are the densities of the compounds at their boiling points. The latter are generally not known. Substitution of densities at a standard temperature generally provide relative diffusion coefficients within 10% of experimental values.

Diffusion coefficient values (measured or calculated) for the compounds of interest are found in Table III. The values observed for the organics in the field cores are much smaller than would be predicted from the product of D and tortuosity values. This suggests that the primary reason for the observed differences in diffusion coefficient values of Cl^- and the organics is the sorption of the organics on the clay.

The effect of sorption on diffusion profiles can be modeled by substituting $D'_{e,c} = D_{e,c}/R$ for $D_{e,c}$ in eqs 2 and 3. R is the retardation factor:

$$R = 1 + \rho_b K_d/n \qquad (6)$$

where ρ_b = soil bulk density (g/cm^3)

and n = soil porosity.

K_d may be determined in laboratory tests, or estimated based on eq 1. Both approaches have been employed here and the results are tabulated in Table III.

The combination of sorption and molecular weight effects leads to estimated total reductions in diffusion coefficient values relative to chloride of from 5 to 50. The $D'_{e,c}$ values estimated using the batch sorption test data are closer to the observed $D'_{e,c}$ values than are those based on eq 1.

FUTURE DOWNWARD MOVEMENT OF THE CONTAMINANTS AT THE SITE

The diffusion model was used to predict the future downward diffusion of the contaminants. For Cl^- a $D_{e,c}$ of 4×10^{-6} cm^2/s was used to simulate migration of Cl^- through the 25 m thick deposit of clay beneath the cell (Figure 7a) for periods of up to 10,000 years. These simulations suggest that flyash-derived Cl^- will begin to arrive in the bedrock at detectable levels ($C/C_o = 0.01$) in about 3,000 years. A steady-state flux of Cl^- to the aquifer will be achieved in about 10,000 years.

These predictions, and those which follow, assume that the contaminant concentrations beneath the clay are maintained at near zero values as the result of groundwater in the bedrock sweeping past the bottom of the clay. They also assume that the mass of contaminants in the flyash is not significantly depleted during the simulation. Because the clay is 25 m thick while the flyash is 15 m thick, and because the Cl^- concentration in the flyash is below its saturation concentration, it is expected that depletion will effect the development of the Cl^- profiles in the clay after a few thousand years, resulting in shallower than predicted profiles.

Predicted diffusion profiles for organic compounds using $D'_{e,c}$ values of 2×10^{-7} and 2×10^{-8} cm^2/s are also given in Figure 7a. The largest value represents the rapidly migrating organics, such as benzene in core 1. The smaller value is representative of the more retarded organic compounds identified in the waste. Breakthrough of organics should be defined on the basis of a lower C/C_o than for Cl^- (e.g. 0.001) because the organic compounds are often of concern at very low concentrations. For example, if benzene exists in solution at 100 ppm at the top of the liner, a $C/C_o = 0.001$ still corresponds to a concentration of 100 ppb, which is high relative to the

levels that should be achieved in drinking water. Thus, in the diffusion modeling, breakthrough of the organics will be specified as occurring at a simulated $C/C_o = 0.001$. When defined in this manner, periods of 5,000 to 15,000 years are required for breakthrough to occur. For the compounds which resist degradation, their steady-state diffusion profiles will only be reached on a geologic time scale. Thus, even though a $C/C_o = 0.001$ may represent a significant concentration, the thick clay deposits at the study site will prevent diffusive transfer to the aquifer for a long period of time. In addition to ensuring a long breakthrough time, the thickness of the deposit also results in a gradual concentration gradient within the clay. This means that, even after breakthrough occurs, the diffusive flux out of the clay will be small.

IMPLICATIONS FOR HAZARDOUS WASTE DISPOSAL AT SITES WITH CLAY LINERS

The thick clay deposit beneath the study site is exceptional in a waste-disposal context. It is becoming increasingly common for hazardous waste cells to be lined with compacted clay of ~ 1 m thickness as a means of isolating the waste from the underlying hydrogeologic domain. The field results obtained in this study can be used, however, to develop predictions regarding diffusive contaminant migration through man-made clay liners.

Figure 7b, produced using the diffusion model described above, indicates that, for a 1 m thick liner, Cl^- will reach a breakthrough concentration of $C/C_o = 0.01$ in approximately 4 years ($D_{e,c} = 4 \times 10^{-6}$ cm^2/s). The diffusive mass flux into the hydrogeologic domain beneath the liner will attain 10% of the eventual steady state value in about 5 years, and reach steady-state in approximately 40 years. Mobile organic compounds such as

benzene will be retarded relative to chloride, but it is again appropriate to calculate breakthrough times for the organics based on C/C_o values of 0.001. When the effective diffusion coefficient for benzene obtained in this study (2 x 10^{-7} cm^2/s) is used to calculate a breakthrough time for a 1 m thick liner, 6 years is obtained. There are many other organic compounds which are as mobile as benzene. Thus, diffusion-controlled breakthrough of the least retarded organic compounds may occur in five years or less. Steady-state conditions will be approached in less than 100 years. For a 1 m thick liner, the concentrations in the waste may be only slightly depleted, and steady-state losses may be substantial.

To obtain an indication of the mass of contaminants which may diffuse through a liner at steady state, consider a 1 m thick liner with an area of 100 x 100 m. Once steady state has been achieved, flux out of the liner is described by Fick's first law:

$$\text{Flux} = n D_{e,c} \frac{dc}{dz} \qquad (7)$$

$D_{e,c}$ is used, rather than $D'_{e,c}$, because at steady state, adsorption equals desorption and there is no net retardation for any species. If the contaminant has a concentration of 1 g/L in the waste at the top of the liner, if $D_{e,c}$ is 1.5 x 10^{-6} cm^2/s, n = 0.4, and if the ground water flow maintains the concentration beneath the liner at a small fraction (e.g. 0.01) of the concentration in the waste, then the steady-state mass transport rate through the liner will be approximately 19 kg/year (1.9 g/m^2/year). For some compounds an annual release of this magnitude would cause a major adverse impact on groundwater quality. For example, 19 kg of benzene has the potential to contaminate 3.8 billion liters of water at the EPA-suggested drinking water limit of 0.005 mg/L.

All of the breakthrough times and the fluxes mentioned above are based on the assumption that advection through the liner is insignificant. In many situations hydraulic gradients across liners are large (i.e. > 1) and therefore average linear velocities across the liners may in fact be significant. For conditions in which the average linear velocity is greater than a few centimeters per year, breakthrough times and mass transfer rates should be calculated using models that include both advection and diffusion, such as those described by Desaulniers et al. (2), Rowe and Booker (19), and Gray and Weber (20). The diffusion analysis presented above, however, thus represents a best-case analysis in that it provides maximum breakthrough times and minimum fluxes. Advection will result in larger values.

Recent designs for liners at hazardous waste disposal sites specify that double liners be used and that a sand or gravel drainage blanket be placed between the two liners. The drainage blanket drains to sumps or other leachate extraction facilities and serves as an interception zone for free leachate that flows through the upper liner. The primary reason for this design is to minimize advection through the lower liner. If the liners are constructed of a porous material such as clay, molecular diffusion will cause contaminants to migrate through the upper liner into the drainage blanket. If the sand or gravel is not dry, downward diffusive migration will continue in the drainage blanket and into the bottom liner. Passage of contaminants through the bottom clay liner by diffusion will be unavoidable and may occur even when the drainage blanket yields no leachate to the collection system. In a diffusion context, this situation is nearly equivalent to the single-liner case. Thus, the fact that a drainage blank is seen to be properly performing its design function, does not necessarily mean that contaminants

are not migrating relatively quickly via diffusion through the bottom liner. The point here is not to argue that properly-constructed double liners with drainage blankets cannot provide a useful degree of additional environmental protection, but rather to emphasize that molecular diffusion is a mechanism of contaminant movement which can not be ignored, even in the design of double liners.

In the foregoing consideration of the implications of diffusion on contaminant migration through clay liners, diffusion coefficient values similar to those found for the cores from the field study were used. Many clay liners at waste disposal sites are formed of compacted local clay, or of local unconsolidated geologic materials mixed with bentonitic clay. Neither the compaction of local clay or bentonite mixtures are expected to produce a material with Cl^- diffusion coefficients more than half an order of magnitude lower than the Tricil clay. In addition, many natural clays and bentonite mixtures contain less solid-phase organic matter and may retard organic compounds less than the Tricil clay. It is expected, therefore, that molecular diffusion through clay barriers will be of general relevance in many clay liner applications.

CONCLUSIONS

The core in which Cl^- travelled the farthest in the five-year period since the wastes were buried matched very closely the results of the diffusion model using a laboratory-measured diffusion coefficient. For the second and third cores, the matches between field data and the model were good for some parts of the cores, while the model overestimated the concentrations for others. These results indicate that the influence of advection is negligible and that diffusion modeling based on laboratory-determined coefficients

provides maximum chloride-migration rates. The fact that the organic compounds migrated a distance of less than 20 cm during five years was justified based on model results using effective diffusion coefficients which were adjusted for the effects of molecular size and adsorption.

The clay deposit at the study site is thick. Therefore, more than 1,000 years will pass before contaminants from the waste will arrive at the aquifer beneath it. When the diffusion model is applied to a 1 m clay liner, however, breakthrough diffusion times for many compounds are less than 10 years and steady state diffusion fluxes can be large. This study suggests that clay liners possessing low permeability will not prevent unadsorbed contaminants from entering, even in the short term, the hydrogeologic domains beneath the liners. Adsorption of organic contaminants may extend the time before breakthrough, but for some of the common priority pollutants, the breakthrough time is only a few decades or less.

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LIST OF TABLES

TABLE 1. CHLORIDE CONCENTRATION DATA

CORE 1		CORE 2		CORE 3		
DEPTH[a]	Cl^- CONCENTRATION[b]	DEPTH	Cl^- CONCENTRATION	DEPTH	Cl^- CONCENTRATION	POROSITY
-15.2 - -7.6	1409(1.1465)	-7.6 - 0.0	2167(1.0000)	-7.6 - -3.8	2100(1.1444)	0.52
-7.6 - 0.0	1229(1.0000)	0.0 - 7.6	1467(0.6770)	-3.8 - 0.0	1835(1.0000)	0.51
0.0 - 7.6	1084(0.8820)	7.6 - 15.2	579(0.2672)	3.8 - 7.6	1545(0.8420)	0.32
7.6 - 15.2	769(0.6257)	15.2 - 22.9	542(0.2501)	7.6 - 11.4	1315(0.7166)	0.36
15.2 - 22.9	779(0.6338)	22.9 - 30.5	715(0.3299)	11.4 - 15.2	297(0.1619)	0.35
22.9 - 30.5	664(0.5403)	30.5 - 38.1	741(0.3419)	15.2 - 19.1	128(0.0698)	0.37
30.5 - 38.1	459(0.3735)	38.1 - 45.7	390(0.1800)	19.1 - 22.9	58(0.0316)	0.38
38.1 - 45.7	379(0.3084)	45.7 - 53.3	252(0.1163)	22.9 - 26.7	36(0.0196)	0.37
45.7 - 53.3	253(0.2059)	53.3 - 61.0	205(0.0946)	26.7 - 30.5	40(0.0218)	0.39
53.3 - 61.0	167(0.1359)	61.0 - 68.6	85(0.0392)	30.5 - 38.1	24(0.0131)	0.39
61.0 - 68.6	105(0.0854)	68.6 - 76.2	32(0.0148)	38.1 - 45.7	14(0.0076)	0.37
68.6 - 76.2	74(0.0602)					
76.2 - 83.8	55(0.0448)					
BACKGROUND	121+/-8	BACKGROUND	213+/-31	BACKGROUND	125+/-10	

[a] cm below the flyash/clay interface

[b] background subtracted concentrations in mg/L and normalized concentrations in parenthesis

TABLE II. ORGANICS CONCENTRATION, TOTAL ORGANIC CARBON (TOC), AND SOIL ORGANIC CARBON (SOC) DATA
ABSOLUTE (ug/L) AND NORMALIZED (in parenthesis)

(a) Core 1

depth interval[a]	benzene	trichloroethene	toluene	ethylbenzene	naphthalene	1,2-dichloropropane	SOC(g/g of soil)	TOC(mg/L)
-15.2 - -7.6	7920 (2.3432)	844.0 (2.3123)	9520 (1.5208)	3320.0 (1.5660)	2352.0 (3.0231)	821.0 (2.7276)	NA[c]	1112.0 (1.2008)
-7.6 - 0.0	3380 (1.0000)	365.0 (1.0000)	6260 (1.0000)	2120.0 (1.0000)	778.0 (1.0000)	301.0 (1.0000)	NA	926.0 (1.0000)
0.0 - 7.6	283 (0.0837)	32.7 (0.0896)	470 (0.0751)	72.9 (0.0344)	23.9 (0.0307)	39.2 (0.1302)	0.010	353.0 (0.3812)
7.6 - 15.2	167 (0.0494)	2.5 (0.0068)	37 (0.0052)	1.3 (0.0006)	0.1 (0.0001)[b]	9.0 (0.0299)	0.013	149.0 (0.1609)
15.2 - 22.8	4 (0.0012)[b]	0.4 (0.0011)[b]	9 (0.0014)[b]	0.8 (0.0004)[b]	0.1 (0.0001)	0.3 (0.0010)[b]	0.012	79.0 (0.0853)
22.9 - 30.5	4 (0.0012)	0.4 (0.0011)	9 (0.0014)	0.8 (0.0004)	0.1 (0.0001)	0.3 (0.0010)	0.013	4.0 (0.0043)

(b) Core 2

depth interval	benzene	trichloroethene	toluene	ethylbenzene	naphthalene	1,2-dichloropropane	SOC(g/g of soil)
-7.6 - 0.0	801 (1.0000)	83.0 (1.0000)	3628 (1.0000)	1503.0 (1.0000)	516.0 (1.0000)	120.0 (1.0000)	NA
0.0 - 7.6	63 (0.0787)	7.3 (0.0880)	393 (0.1083)	168.0 (0.1118)	109.0 (0.2112)	11.5 (0.0958)	0.010
7.6 - 15.2	300 (0.3745)	5.8 (0.0699)	175 (0.0482)	6.6 (0.0044)	0.2 (0.0004)	16.5 (0.1375)	0.013
15.2 - 22.8	4 (0.0054)[b]	0.4 (0.0048)[b]	9 (0.0025)[b]	0.8 (0.0006)[b]	0.1 (0.0002)[b]	0.3 (0.0025)[b]	0.009

(c) Core 3

depth interval	benzene	trichloroethene	toluene	ethylbenzene	naphthalene	1,2-dichloropropane	SOC(g/g of soil)
-7.6 - -3.8	620 (3.7126)	67.0 (2.9386)	2230.0 (1.8740)	755.0 (1.9162)	76.0 (3.2759)	198.0 (2.6757)	NA
-3.8 - 0.0	167 (1.0000)	22.8 (1.0000)	1190.0 (1.0000)	394.0 (1.0000)	23.2 (1.0000)	74.0 (1.0000)	NA
3.8 - 7.6	122 (0.7305)	6.5 (0.2851)	166.0 (0.1395)	7.6 (0.0193)	0.2 (0.0086)[b]	1.9 (0.025)	0.007
7.6 - 11.4	36 (0.2156)	0.4 (0.0175)[b]	0.9 (0.0008)	0.1 (0.0002)[b]	0.2 (0.0086)	0.3 (0.0041)[b]	0.010
11.4 - 15.2	3 (0.0192)[b]	0.4 (0.0175)	0.5 (0.0004)[b]	0.1 (0.0002)	0.2 (0.0086)	0.3 (0.0000)	0.013

[a]distance below the interface (cm)

[b]at or below the minimum detectable concentration

[c]not analyzed

TABLE III. SORPTION AND DIFFUSION COEFFICIENT VALUES

COMPOUND	FREE-SOLUTION DIFFUSION COEFFICIENT D (cm^2/s)	ORGANIC CARBON PARTION CONSTANT K_{oc}	CALCULATED PARTITION COEFFICIENT[f] $K_{d,calc}$	ORGANIC CARBON RETARDATION FACTOR[g] R_{oc}	CALCULATED DIFFUSION COEFFICIENT[h] D'_{calc} (cm^2/s)	OBSERVED PARTITION COEFFICIENT[i] K_d	RETARDATION FACTOR[j] R	CALCULATED DIFFUSION COEFFICIENT[k] D'_{calc} (cm^2/s)	OBSERVED DIFFUSION COEFFICIENT[l] $D'_{e,o}$ (cm^2/s)
chloride	2×10^{-5} [a]	0.0	0.0	1.0	5×10^{-6}	0.0	1.0	5×10^{-6}	5×10^{-6}
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]	[redacted]
1,2-dichloro-propane	8×10^{-6} c	48.[d]	0.48	3.1	6×10^{-7}	ND[m]	ND	ND	1×10^{-7}
ethylbenzene	6×10^{-6} b	870.[e]	8.70	39.	4×10^{-8}	62.	269.	6×10^{-9}	2×10^{-8}
naphthalene	6×10^{-6} c	940.[d]	9.40	42.	4×10^{-8}	ND	ND	ND	2×10^{-8}

[a] from Li and Gregory (16).

[b] from Binoli and Witherspoon (17).

[c] calculated using Equation 5 and $D = 7 \times 10^{-6}$

[d] from Mabey et al. (21).

[e] using $\log K_{oc} = \log K_{ow} - 0.21$ (Kariokhoff (22)) and $\log K_{ow} = 3.15$

[f] $K_{d,calc} = K_{oc} \times SOC$
$= K_{oc} \times 0.01$

[g] $R_{oc} = 1 + (\text{soil bulk density} \times K_{oc} \times SOC) / \text{porosity}$
$= 1 + (1.6 \times K_{oc} \times 0.01) / 0.37$

[h] $D'_{calc} = D \times \tau / R_{oc}$
$= D \times 0.25 / R_{oc}$

[i] from the batch sorption experiments at ~1000 ug/L

[j] $R = 1 + (\text{soil bulk density} \times K_d)/\text{porosity}$
$= 1 + (1.6 \times K_d)/0.37$

[k] $D'_{calc} = D \times \tau / R$
$= D \times 0.25 / R$

[l] measured in core 1

[m] ND = not determined.

LIST OF FIGURES

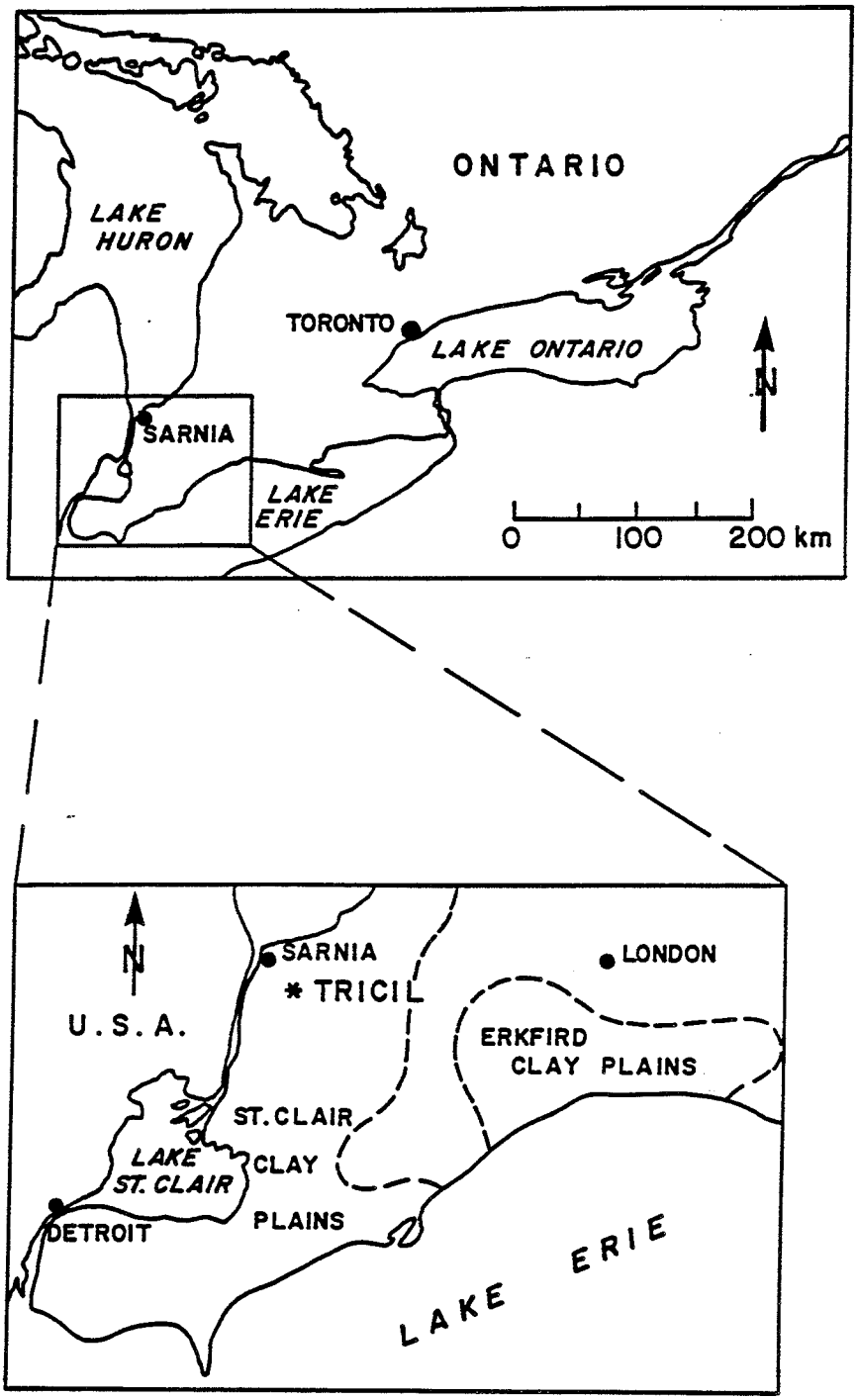


Figure 1. a) Regional map showing the location of the site on the St. Clair clay plain; b) Sarnia area map.

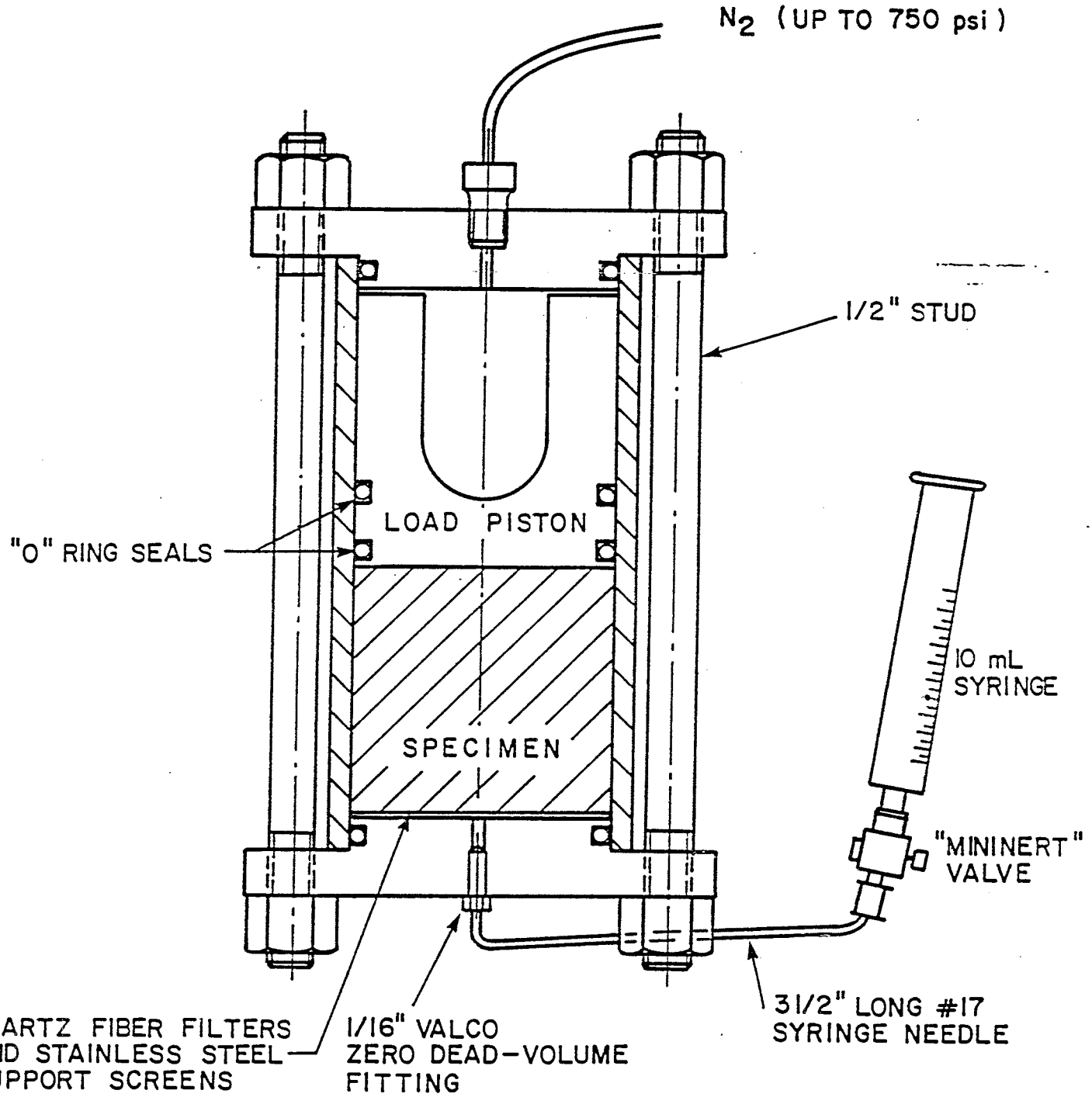


Figure 2. Cross-sectional view of one of the consolidometers.

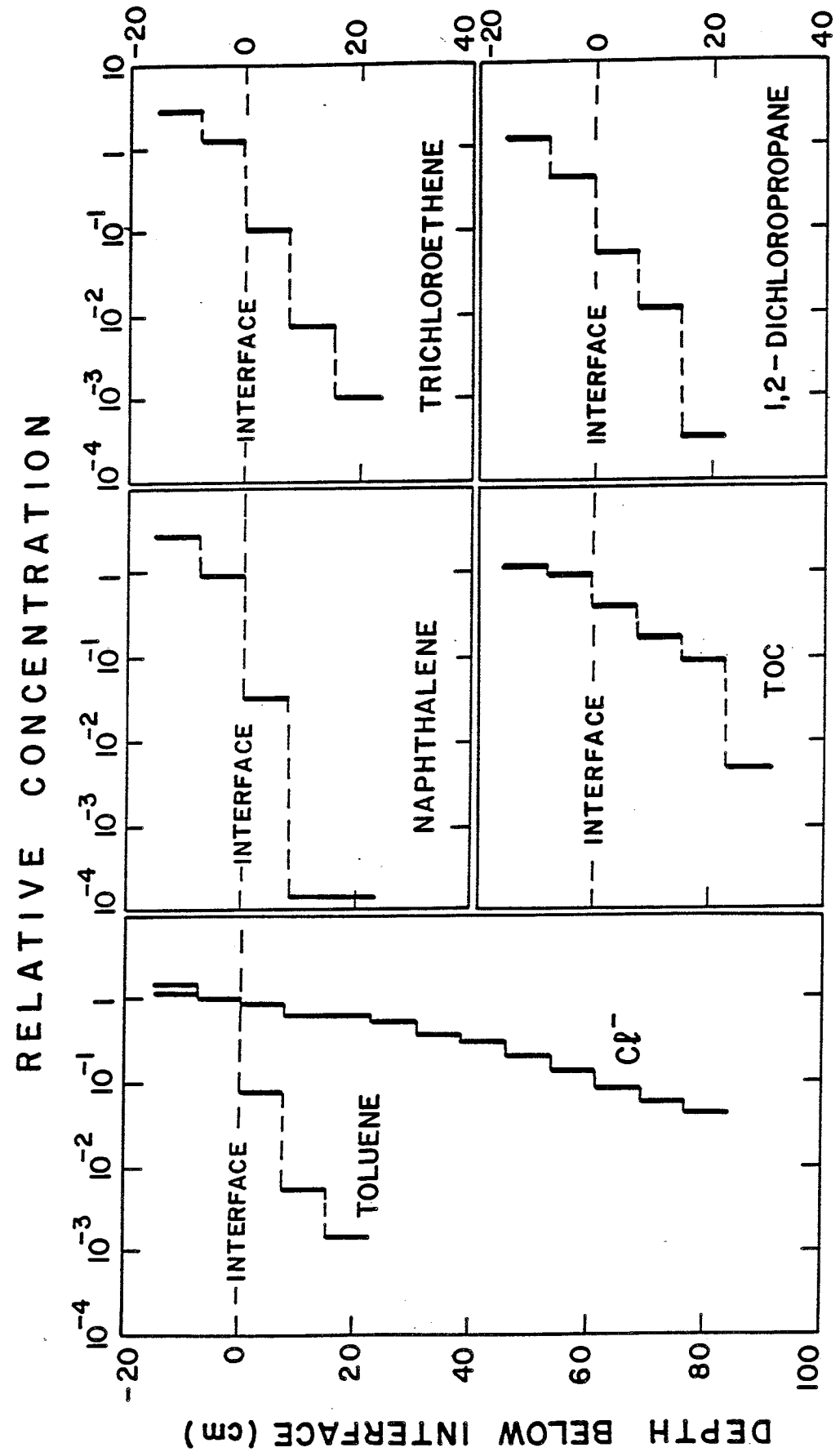


Figure 3. Semi-log plots of chloride and several organics for core 1.

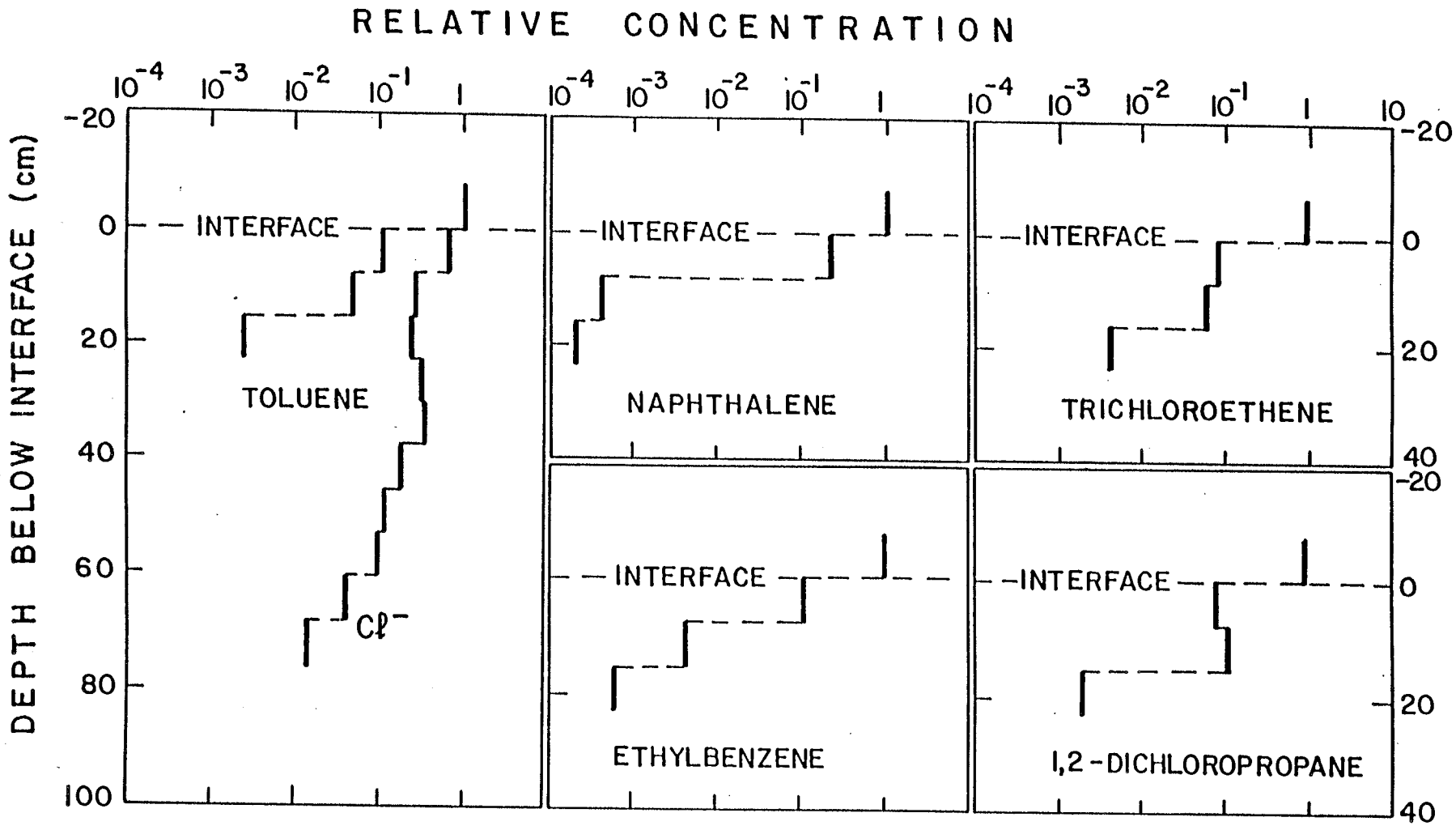


Figure 4. Semi-log plots of chloride and several organics for core 2.

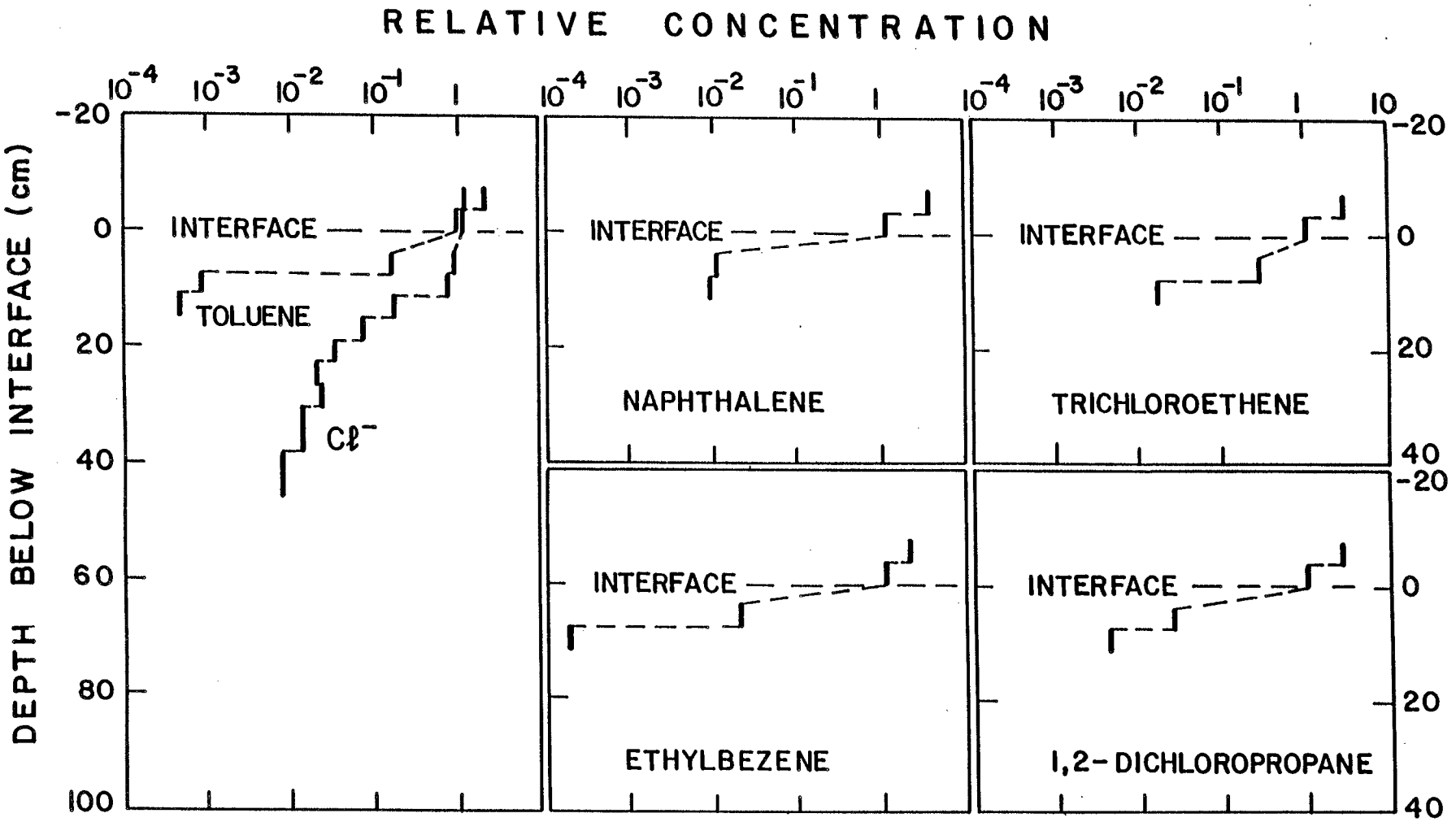


Figure 5. Semi-log plots of chloride and several organics for core 3.

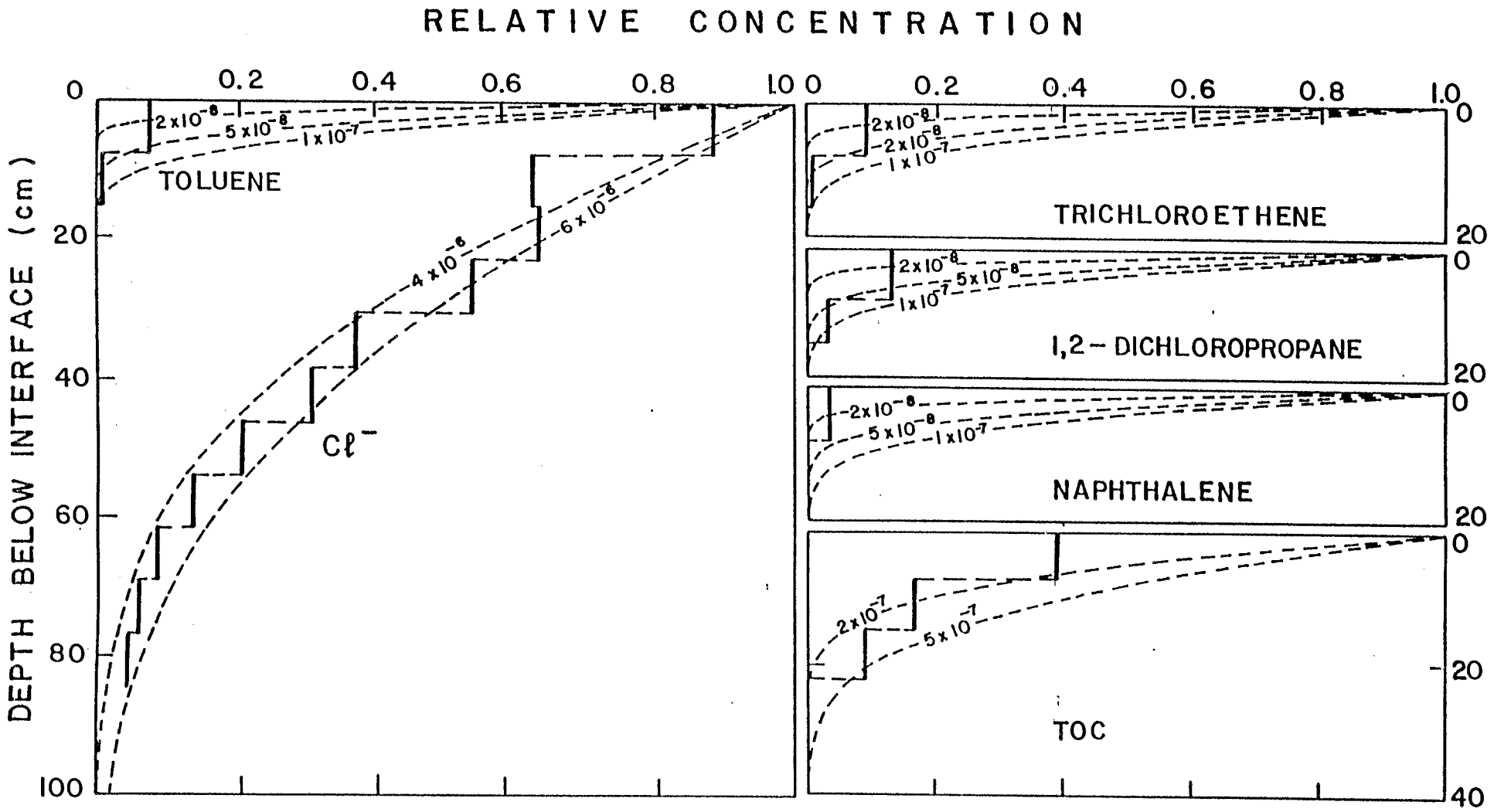
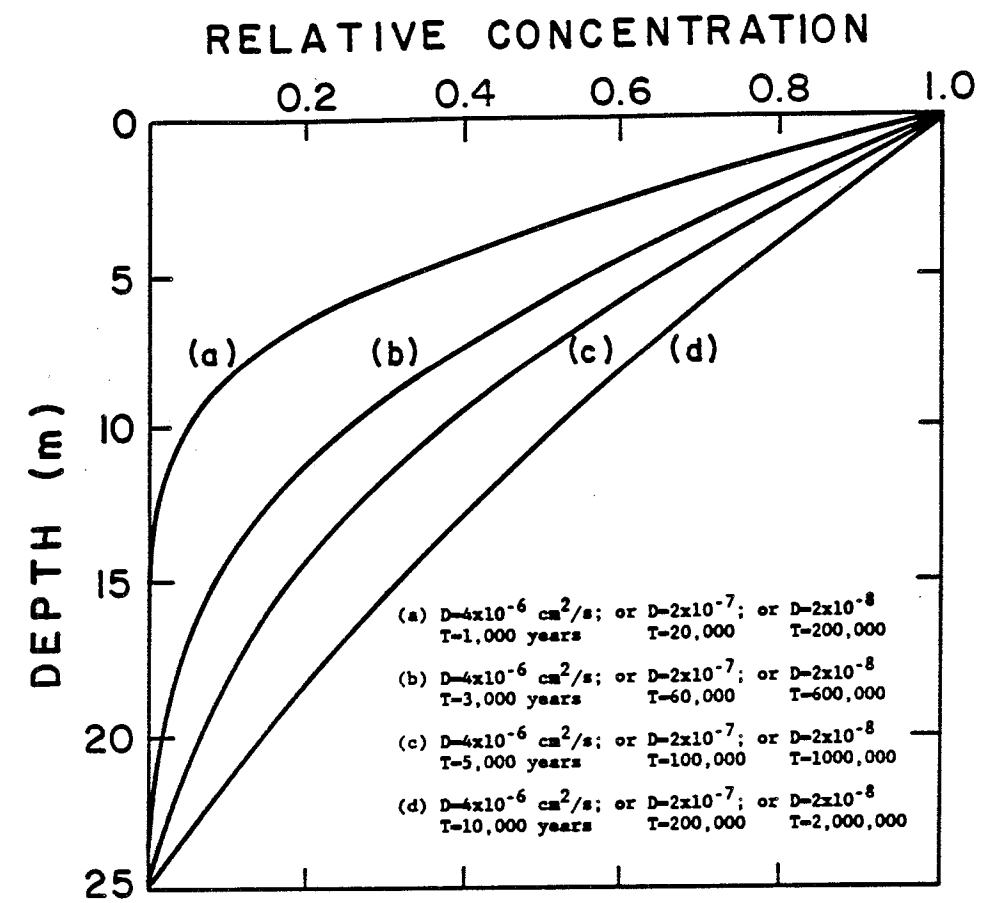


Figure 6. Linear plots of chloride and several organics in core 1, along with simulation data. Time = 1800 days and diffusion coefficients are indicated on the figure (cm^2/s).



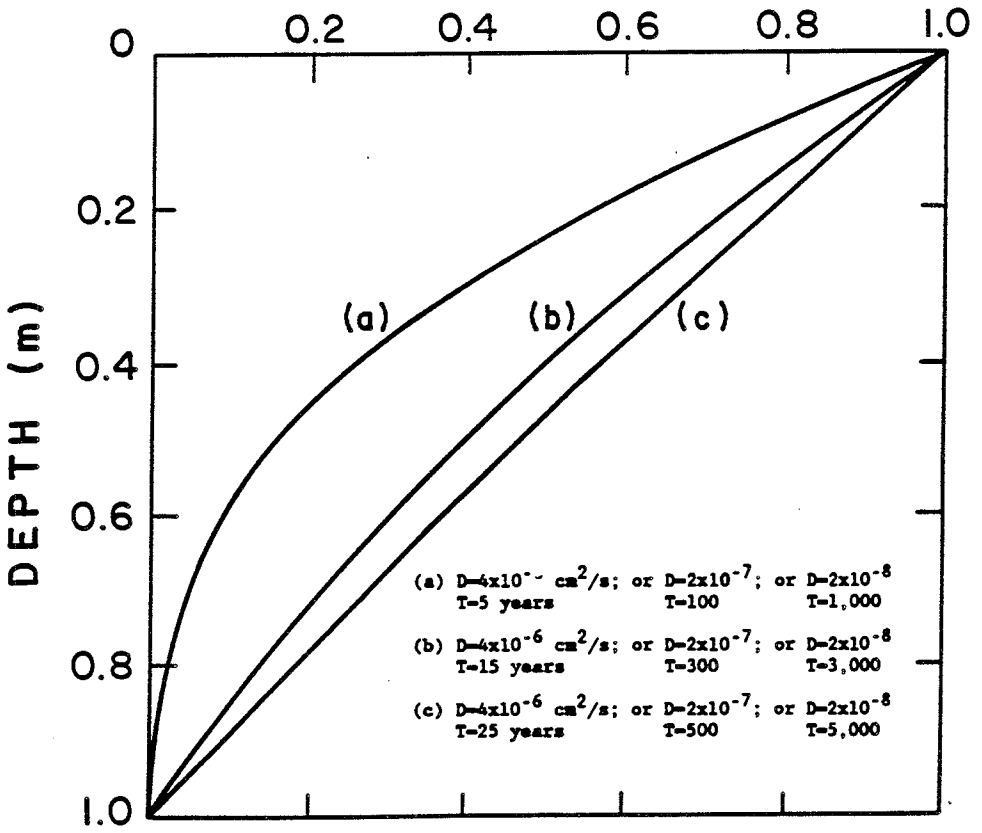


Figure 7. Simulations of diffusion into 25 m and 1 m thick clay liners using the times (years) and diffusion coefficents (cm^2/s) indicated in the figure.

Lecture 4

Hydrogeological Concepts and Criteria for Waste Disposal

HYDROGEOLOGIC ASPECTS OF LANDFILL IMPACTS ON GROUNDWATER AND SOME REGULATORY IMPLICATIONS

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ABSTRACT

For more than 15 years in Ontario hydrogeologic factors have been included in considerations of site selection and operation of municipal landfills. In the early years little was known regarding the impacts of landfills on groundwater, and therefore the hydrogeologic concepts used in landfilling were largely intuitive. As more has become known about landfill impacts on groundwater, the hydrogeologic concepts have evolved. Field, laboratory and modelling research conducted during the past five years provides impetus for changes in the perception of the manner and the degree to which landfills can impact groundwater. The organic contaminants in leachate present the greatest threat to groundwater quality, with small amounts capable of causing serious long-term aquifer contamination. There are many thousands of organic compounds being produced, many of which are persistent in the subsurface and pose potential health hazards in drinking water. Some of these are relatively mobile in aquifers. Off-site migration of contaminants in groundwater will occur at both attenuation-type landfills and at landfills with liners and leachate collection systems. Attenuation processes can provide on-site or near-site attenuation to near or below drinking-water limits for most of the common major-ion and metal contaminants. However, the front of a leachate plume marking the safe drinking-water limit for mobile organic contaminants can extend far from attenuation-type landfills. Molecular diffusion results in contaminant breakthrough from lined landfills, generally within a few decades or sooner. The choice of a relatively good hydrogeological setting for a landfill will result in very slow contaminant migration and therefore in a centuries or longer delay in the first arrival of these contaminants at off-site locations. This choice should also result in a relatively low long-term maximum contaminant loading rate to offsite groundwater or surface water. These considerations invite an updating of water quality standards and incorporation into landfill regulations of both explicit consideration of time to first offsite arrival of contaminants and of eventual loading rates for contaminants to offsite groundwater or surface water. Commitment to further research into better methods for impact prediction is needed.

INTRODUCTION

In Ontario hydrogeologic factors play an important role in the selection and operation of sanitary landfills. This has been the case for the past 15 years or longer. The manner in which hydrogeologic factors enter into landfilling considerations depends greatly upon the type of leachate control system used at the landfill, and especially upon the conceptual model that is used to predict landfilling effects on groundwater. Much of what is now known about these effects has been learned through research conducted during the past ten years and particularly during the past five years.

This paper summarizes our impressions of the major findings of this most recent period of research. We attempt to identify research findings that should cause evolution in conceptualizations of hydrogeologic factors in landfilling. Of particular interest in this discussion are issues pertaining to the attenuation and diffusion of contaminants in the groundwater zone and to implications with respect to the lack of tendency for plumes to achieve steady-state shapes near landfills. A major finding is that attenuation is effective for many inorganic landfill contaminants, but not for the many potentially hazardous organic contaminants that are mobile and persistent. The recent research leads to the prognosis that nearly all municipal landfills in Ontario will eventually cause degradation of groundwater quality beyond the property boundaries of the landfill sites. If groundwater flow paths extend from the landfill to a river, marsh or lake, contaminants from the landfill will eventually be transported by groundwater to the surface-water environment. To a large degree consideration of the issues of landfill impacts on groundwater should be focused on the time predicted for hazardous contaminants to travel from the landfill to offsite locations and on the ultimate contaminant loading rate to these locations, and to a much lesser degree on a dependance on attenuation in the groundwater zone.

Leachate typically has numerous organic contaminants that in the groundwater zone are persistent and relatively mobile. In some jurisdictions outside of Canada many of these contaminants have recently been designated as hazardous contaminants. Some have been assigned parts per billion limits in drinking water standards. The chronic effects of many of these contaminants on human health are unknown. There is not much doubt that when these contaminants migrate from landfills to potable groundwater offsite, actual or potential users of this water will regard the groundwater resource as having become damaged beyond normal use. Even if the offsite contamination zone does not have contaminants listed in drinking water standards or guidelines but has above-background levels of other organic compounds, it is unlikely that users of this water will agree that it is drinkable even if regulatory agencies regard the contaminants as representing no significant hazard.

ORGANIC CONTAMINANTS

In the past much of the focus of landfill hydrogeology has been on inorganic constituents in leachate plumes. More recently organic contaminants are of concern because of increased public and scientific awareness of their hazardous nature, their widespread use and their unique properties. Improved analytical detection methods have shown the ubiquitous nature of organic compounds in leachate. In a hydrogeological context organic contaminants are particularly troublesome.

Drinking-water standards for most organic compounds are low because low dissolved concentrations in groundwater used for water supply represent potential health risks. Conversely, drinking water standards for many relatively harmless inorganic ions, such as chloride (Cl^-) and sulfate (SO_4^{2-}), are based on aesthetic factors such as taste. Because the drinking water standards for many organics are low, only small quantities are required for major groundwater contamination. For example, 5 kg of 1,2-dichlorobenzene could potentially contaminate one-half billion litres of groundwater to 4 times the Ontario Provincial Water Quality Objective of 2.5 µg/L (1 µg = 10^{-6} g). This quantity of groundwater would supply 40 normal Ontario households for approximately 50 years. Only 0.12 kg of pentachlorobenzene would contaminate the same volume of water to 8 times the Provincial Water Quality objective of 0.03 µg/L.

The potential for a very small amount of an organic chemical to impact a large volume of groundwater can be shown in another way. Consider a hypothetical contaminant plume that is 1 km long, 10 m deep and 100 m wide. The plume contains 1,2 - dichlorobenzene at an average concentration of 25 µg/L, which is well above the drinking water objective of 2.5 µg/L. The total amount of 1,2 - dichlorobenzene in the plume is only 10 kg, or when expressed as an industrial liquid product is only 7.7 L. A conclusion that can be derived from calculated examples such as these is that severe groundwater contamination may be caused by very small inputs of industrial organic chemicals to the groundwater zone.

The above examples are for two organics of the possible 40 to 100 organic compounds commonly identified in landfill leachate (Reinhard et al., 1984; Cherry et al., 1985). It is also estimated that less than 10% of the total mass of dissolved organic carbon in landfill leachate plumes consists of identifiable compounds (J.F. Barker, personal communication). Therefore the full potential effect of organics in leachate is not known. Attempting to regulate input to a municipal landfill will not be effective due to the large volume of solid wastes which must be disposed of

and the small, diverse sources of organic compounds in this waste. We must accept that toxic industrial organic compounds will continue to be present in most municipal landfill leachate.

Some of the common organic compounds found in leachate produced from normal municipal refuse at several landfills throughout southern Ontario are given in Table 1. Also included in this table are the Ontario Provincial Water Quality Objectives. The list of detected organics is not complete; it includes the commonly encountered, more mobile compounds which can be reliabily determined. It is apparent that the Ontario Water Quality Objectives are not adequate to deal with the commonly detected organics in landfill leachate. The U.S. Environmental Protection Agency currently has over 120 organic compounds on its "Priority Pollutant" list, and yet acknowledges that this list is incomplete. Although new objectives have recently been set for chlorinated benzenes and chlorinated phenols (Ministry of the Environment News Release, 1986) more attention must be paid to setting criteria for many other organics that are commonly found in landfill leachate and in other types of waste that frequently impact on groundwater.

Many organic contaminants do not undergo significant attenuation in the subsurface. At several study sites in Ontario organic compounds, such as dichlorobenzenes, have been detected 800 m from landfills sited on sandy aquifers (Reinhard et al., 1984). Obviously such a travel distance will be different at each landfill site and depends on hydrogeological conditions and the properties of the individual compounds. At the North Bay landfill study site (Cherry et al., 1985) the spatial distribution of the total dissolved organic carbon (TOC) and chloride are very similiar, as shown in Figure 1. This indicates that little attenuation of many of the refuse-derived organic compounds is occurring in the sand aquifer. Although sorption and biodegradation of some of the organic compounds in landfill leachate may occur at any particular site, there will be compounds which will be conservative in the groundwater flow system. Attenuation is discussed further in the following section.

This discussion has focused on dissolved organic contaminants and has not addressed non-aqueous phase liquids (NAPLs), such as chlorinated solvents. These compounds in product form are immiscible in water and are more dense than water, therefore they can rapidly migrate into the subsurface as a seperate phase and act as a long-term source for dissolved contaminants. At present it is not possible to predict the migration of NAPLs in the subsurface.

ATTENUATION

Contaminants in the groundwater zone may be attenuated by the following processes: dispersion, sorption, and biodegradation (including biotransformation). Although these processes are all generally viewed as resulting in attenuation, each process causes different effects. Dispersion causes mixing of contaminated and uncontaminated water and is the only process causing mixing in the groundwater zone. Dispersion causes maximum concentrations in contaminant plumes to decline and, at the same time, it causes the total mass of contaminants to occupy a larger portion of the groundwater zone than would otherwise be the case. Dispersion can be beneficial or non-beneficial depending on the circumstances.

Figure 2 shows conceptual examples of a landfill plume for a non-retarded, non-biodegradable contaminant in a sand or gravel aquifer underlying a leaky aquitard or leaky liner. Such a plume can be defined on the basis of isolines of relative concentration, or 'C/Co'(concentration 'C' of a contaminant in the plume at some distance from the landfill divided by the average concentration 'Co' of the same contaminant in leachate in the shallow groundwater zone directly beneath the landfill). Figure 2, Case A shows this idealized plume without dispersion effects (i.e. no mixing). In this case the plume geometry is determined by the groundwater flow net. In Figure 2, Case B the plume exterior extends vertically and longitudinally beyond the Case A plume because of dispersion . The edge of the plume is defined as the concentration isoline for a very low concentration of the contaminant. In Figure 2, Case C the plume is somewhat thicker but considerably shorter than in Case A. In this case the exterior or front of the plume is defined using a much higher contaminant concentration for the concentration isoline. These diagrammatic examples illustrate that plumes in sand or gravel aquifers can be larger or smaller depending on our choice of concentration for delineating the exterior boundary of the plume. In practice, exterior boundaries of plumes are normally delineated based on 1) the apparent background concentration of the contaminant being considered, 2) the analytical detection limit for the contaminant, or 3) the drinking water standard for the contaminant. In Figure 2, Case C could be viewed as a chloride or sulphate plume based on a drinking-water guideline value of 250 mg/L, whereas Case B could be considered as a compound such as hexachlorobenzene with an Ontario guideline value for maximum concentration) of 0.0065 µg/L (Ministry of the Environment News Release, 1986).

The concentrations of mobile major ions such as Cl^-, SO_4^{2-}, Na^+ and Fe^{2+} in landfill leachate within and directly beneath landfills are rarely more than 10 times the guideline limits for drinking water. If dispersion causes these leachate constituents to decline by a factor of 10 or 20, a plume defined on the drinking-water limit concentration of these constituents will be much smaller than if its full extent were to be delineated on the

basis of trace-level organic compounds. Plumes with fronts delineated by high relative concentrations such as C/Co = 0.1 (or 10%) approach a full steady-state shape much more rapidly than plumes with fronts based on the very low relative concentrations pertinent to many trace-level organic contaminants. For the case of a C/Co = 0.1 plume, isolines for a non-reactive contaminant such as Cl^- show that the lateral distance from the landfill to the front of the steady-state plume in a horizontal sand and gravel aquifer may be a few kilometres or less if conditions are favourable. Distances of a few hundred meters may be possible but a few tens of meters is generally too small to achieve the steady-state condition. Thus, buffer zones of only several tens of meters at landfill sites have little chance of effectively attenuating contaminants such as Cl^- or Fe^{2+}. The specific distance required will depend strongly on factors such as the dispersion coefficients, the bottom area of the landfill and the leachate flux. Recent research on dispersion in sand and gravel aquifers shows that both longitudinal and transverse dispersion coefficients are generally much smaller than was previously thought (Sudicky, 1986). The smaller the dispersion coefficients, the larger will be the lateral distance to the front of steady-state plumes.

For a simple case where the concentration of the contaminant in groundwater at the landfill is steady with time or fluctuating mildly about a steady mean, the plume will achieve steady-state for a non-reactive contaminant in the manner represented in Figure 3. The concept of steady-state plumes is discussed in detail by Germain (1981). If the property boundary for the landfill site is situated beyond the front of the steady-state plume then the plume can be thought of as being fully attenuated on site. In this hypothetical case with extended landfill property boundaries, contaminants well represented by the C/Co = 0.1 isoline do not pose a threat to the quality of groundwater beneath neighbouring properties.

For mobile, non-degradable contaminants with much lower drinking-water limits and relatively high concentrations at the landfill, the plume will not attain a steady-state front within even a reasonably extended property boundary. For $C/Co \ll 0.1$, the distance to a steady-state front will be great, many kilometers or even tens of kilometers from the site boundary if the aquifer extends such a distance. The development of off-site impact on groundwater then is just a matter of time.

Because the contaminants that are most likely to cause groundwater to become impotable are generally those in the $C/Co \ll 0.1$ category (i.e. organics that may cause potential adverse health effects in drinking water at concentrations of tens of parts per billion, or µg/L, or less), it is generally unreasonable to select a landfill site based on any expectation that attenuation will prevent offsite groundwater from becoming

impotable. Adsorption causes many contaminants to travel more slowly than constituents such as Cl-, but the ultimate spatial development of the plume does not differ provided that contaminant input continues. Only the time necessary for plume development is different.

In some circumstances some organic contaminants in the C/Co << 0.1 category undergo biodegradation. When biodegradation of a contaminant occurs at a significant rate the steady-state distance may be very small, thereby resulting in onsite attenuation of the contaminant. Unfortunately, biodegradation is not of much practical importance in the selection of landfill sites because not all contaminants biodegrade and because prediction of biodegradation is very unreliable at present.

MOLECULAR DIFFUSION

To cause delay in the time to first arrival offsite of potentially hazardous contaminants and to minimize the long-term flux of contaminants to offsite groundwaters, it is generally necessary to locate landfills on unfractured clayey deposits or on a liner of compacted clay. In this discussion the aquitard shown in Figure 2 is now considered to be unfractured clay. The hydraulic conductivity 'K' of this clay is assumed to be 10-9 cm/s, which is at the lowest end of the range of K for natural or compacted clay in Ontario. K values specified for compacted clay liners are generally higher, in the range of 10-7 or 10-8 cm/s.

Even though this clay layer beneath the landfill has a K value at the lowest end of the range for any clay that one can find or construct in Ontario, contaminants will move through the clay. This movement will be governed by molecular diffusion, a process whereby dissolved chemical constituents move from locations of higher concentration to ones of lower concentration. Diffusion occurs in porous media regardless of the presence or absence of Darcian groundwater flow.

In a clay layer that is thin, such as a compacted clay liner with a thickness of 1m, diffusion will cause mobile contaminants such as chloride to arrive at the bottom of the liner within about 6 years. This will generally be the case regardless of whether or not water flow is downward or upward through the liner. An example of leachate migration through a low K natural clay in the Sarnia area (Johnson et al., in press) is shown in Figure 4. This example was obtained by taking vertical cores at the bottom of a deep waste disposal pit situated on a thick deposit (45m) of clayey glacial till. The contaminant profiles developed during a 5 year period since the waste pit was filled. Figure 4 shows that relatively mobile, hazardous organic contaminants such as toluene and benzene have moved slower than Cl but nevertheless at a very

significant rate. The dashed lines represent predictions calculated using a simple diffusion model (Fick's Second Law).

At this site the natural clay beneath the waste pit is so thick that many centuries or more will pass before contaminants arrive in the bedrock aquifer beneath the clay. The rate of advance of a diffusion front diminishes rapidly with distance of the front from the contact between the waste and the clay. Thus, much longer delay times can be attained from a doubling of the thickness of clay liners. The liner provides for a delay in contaminant arrivals but does not cause much attenuation of many hazardous organic contaminants.

In the United States, the U.S. Environmental Protection Agency shows no recognition of the existence of molecular diffusion as a contaminant-migration process, even in its most recent regulations pertaining to disposal sites and liners. No recognition of diffusion exists in regulations in Canada.

Molecular diffusion was first recognized as a significant process in low-permeability geologic media eleven years ago by a British hydrogeologist (Foster, 1975). Studies of molecular diffusion in natural clay in Canada were first published ten years ago by Goodall and Quigley (1977) and Day (1978). These and more recent studies by Desaulniers et al. (1981, 1986), Crooks and Quigley (1986), and Myrand (1987) have clearly established the rates at which diffusion of a variety of contaminants occur in natural Ontario clay deposits. Similar rates of diffusion occur in compacted clay liners. It is now an opportune time for consideration of molecular diffusion to be included in regulations for landfills in Ontario. In addition to the downward migration of contaminants through clay at the bottom of landfills, diffusion can cause contaminants to migrate upward through compacted clay cover layers on landfills.

LANDFILL LEACHATE CONTROL SYSTEMS

Conceptual designs for municipal landfills based on the subsurface migration of leachate or the engineered control of leachate can be classified in two basic types:

- landfills dependent primarily on attenuation in the hydrogeologic domain
- landfills dependent primarily on engineered liners and leachate collection systems.

In our discussion 'system' includes both the engineered parts of the landfill and the hydrogeological regime.

Hydrogeological conditions affecting leachate control systems include local water-table elevations and fluctuations, direction and magnitude of hydraulic gradients, soil hydraulic conductivity,

geology and the attenuative properties of the underlying materials (Freeze and Cherry, 1979).

Attenuation Systems

At an attenuation-type landfill the leachate concentrations in the groundwater around the landfill are supposed to be reduced to acceptable levels at some designated point of concern (often the site boundary) through attenuation by the processes of dispersion, sorption, and biodegradation. The attenuation is expected to occur naturally in the hydrogeologic domain. Engineered leachate collection facilities may be present but are not expected to prevent a considerable amount of the leachate from entering the groundwater zone.

In the undated document, 'Guidelines for .... Landfilling Sites in Ontario', the Ministry of the Environment states that liners "should normally be used only when no alternative is available" and that "as a general rule, unless it is absolutely unavoidable, it is better not to collect and treat leachate" - that is, the Ministry of the Environment presently prefers attenuation-type landfills. It does so with the intention that groundwater on property adjacent to any landfill should be kept suitable for "reasonable use", where reasonable use usually refers to domestic consumption (Ontario Ministry of the Environment, 1986).

The advantages of this type of system are generally lower capital cost and lower operating costs in that less leachate needs to be collected and passed through sewage treatment plants. The treated leachate is normally discharged to rivers or lakes where it may cause surface-water contamination. At landfill sites well suited for attenuation in the groundwater zone, considerable attenuation may be achieved within the site property. At a very good attenuation site the eventual migration offsite of mobile hazardous contaminants may well represent minimal environmental loading when compared to landfills dependent on leachate collection, treatment and discharge to surface water.

The main disadvantage of this system is that low concentrations of some contaminants from the landfill can be expected to eventually spread offsite in concentrations higher than their drinking water limits. Attenuation-type landfills can only be evaluated in terms of their desirability if reliable predictions of their impact can be made. As yet there is considerable uncertainty associated with even the most careful predictions of the ultimate severity of offsite contaminant migration in groundwater.

Leachate Collection Systems

The alternative to the natural attenuation system is the

engineered landfill with a leachate collection system, where the quantity of leachate escaping from the site is minimized. If the landfill is situated on a thick, relatively-impervious clayey deposit, then this system normally does not need an engineered liner but only a leachate collection system. If the site has significant permeability, then it will require an engineered liner constructed of compacted clay or a polymeric membrane. Collection pipes or drains are used to collect the leachate from a permeable leachate collection layer which overlies the liner. The leachate is treated if necessary before discharge (McGinley and Kmet, 1984). The ultimate disposal of the leachate, treated or untreated, will usually be to surface waters.

A properly designed, constructed and maintained system may reduce leachate discharge to near zero, but a small amount of contaminants will always reach the groundwater zone by molecular diffusion through natural or compacted clay and through small holes and imperfections in the liner.

The advantages of this kind of system are that it can be used in almost any hydrogeological setting, and that almost all of the leachate is collected and disposed of in a controlled or otherwise known manner.

The disadvantages of this system are that the collection systems are costly and that their long-term reliability is unknown. Collection and treatment of leachate may be necessary for centuries. The treatment of toxic chemicals in the leachate or the lack of facilities for such treatment can be limiting factors. At present, if the leachate is treated at all, the treatment occurs at municipal sewage plants not designed to handle such wastes.

Consideration of Hydrogeological Setting

The hydrogeological setting of a landfill refers to the entire groundwater flow system in the vicinity of the landfill. The effects of the local hydrogeological setting upon landfill operations can be very significant. For example, a study by Massmann and Freeze (1987) indicates that requiring that a landfill is located on thick clay deposits may do more to reduce the risk of environmental contamination than any other regulatory factor. In the attenuation type landfills mentioned above, the hydrogeological setting should be a dominant factor in the site selection process.

Attention has long been focused upon the water table as a major factor in landfill site selection and design. Regulations in many provinces require that the landfill base be situated above the water table. The concept of unsaturated-zone landfilling was developed in California in the 1950's and was widely adopted across much of North America, even though the moist eastern climate often made unsaturated zone landfilling undesirable in

these areas (McGinley and Kmet, 1984). In order to situate a landfill above the water table, the unsaturated zone must be several meters thick - this allows a sufficient thickness of soil for the disposal pits to be excavated above the water table. In Ontario, such a thick unsaturated zone is generally associated with permeable sand and gravel deposits, or with deeply fractured clays or permeable, fissured bedrock.

When landfill siting guidelines or regulations require or suggest that preference in the site selection be given to unsaturated zone sites, then the selection process is driven in an hydrogeologically inappropriate direction. Unweathered clays in Ontario generally have a shallow water table and although they are often excellent sites for landfills, they would be excluded if regulations requiring above-water-table landfilling were to be followed.

IMPLICATIONS

1) There are vast numbers of potentially dangerous chemicals being produced and disposed of today, and despite control efforts many are finding their way into landfills. As contamination problems related to landfills become more serious most provinces will likely follow the lead of Ontario in specifying that contaminant concentrations in leachate plumes meet specific objectives at some designated point(s) of concern.

2) A considerable number of the chemical compounds on the list of 'priority pollutants' designated by the U.S. Environmental Protection Agency are relatively persistent and mobile in many common types of groundwater systems. Few of these and other potentially hazardous compounds that are prone to causing groundwater contamination are included in the most recent Ontario Drinking Water Objectives and the Provincial Water Quality Objectives. The existing Objectives therefore are not an appropriate basis for development of expectations regarding the significance of offsite migration of contaminants from Ontario landfills.

3) It is not feasible to prevent small but nevertheless significant quantities of hazardous wastes from entering essentially all municipal landfills. Because small quantities of many common hazardous organic compounds may cause severe groundwater contamination, municipal landfills should be regarded as significant potential threats to groundwater quality.

4) At the present time, landfilling is an unavoidable means of disposing of most municipal waste. Also, eventual offsite migration of contaminants is an unavoidable consequence of landfilling in nearly all types of hydrogeological settings. It is

desirable that landfills be situated in hydrogeologic settings where impacts due to offsite contaminant migration will be minimal because the groundwater is of little or no present or future value, or where the time to first offsite arrival of contaminants is very long and the maximum eventual offsite flux of contaminants is small. Time is a factor that should be incorporated into landfill regulations or guidelines.

5) Any regulation or guideline requiring or advocating unsaturated -zone landfills is a relic of the past and can be expected to do more harm than good.

6) Compacted clay liners will not prevent contaminants from reaching groundwater outside of the landfill. Breakthrough of relatively mobile contaminants in properly-designed compacted clay liners will occur due to molecular diffusion after only several years.

7) The concern prompted by known or perceived health effects due to trace-level organic contaminants in drinking water, combined with recent research findings indicating persistence and mobility of many of these contaminants and the relative ineffectiveness of attenuation processes on these contaminants in the groundwater zone, invites regulatory adaptation to recent research results in Ontario and elsewhere in Canada.

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Table 1. Commonly detected organic contaminants in municipal landfill leachate plumes[1] and water quality objectives.

	Ontario Objective (µg/L)
* Aromatic Hydrocarbons	
benzene	-
toluene	-
ethylbenzene	-
m/p-xylene	-
o-xylene	-
trimethylbenzene	-
napthalene	-
* Chlorinated Benzenes	
chlorobenzene	-
1,2-dichlorobenzene	2.5
1,4-dichlorobenzene	4.0
* Volatile Halocarbons	
1,1,1-trichloroethane	-
trichloroethylene	-
tetrachloroethylene	-
carbon tetrachloride	-
chloroform	-
* Phenols	
phenol	2.0
methylphenol isomer	-
ethylphenol isomer	-
chlorocresol isomer	-
* various Carboxylic Acids	-

[1]Sources : Cherry et al., 1985; Reinhard et al., 1984

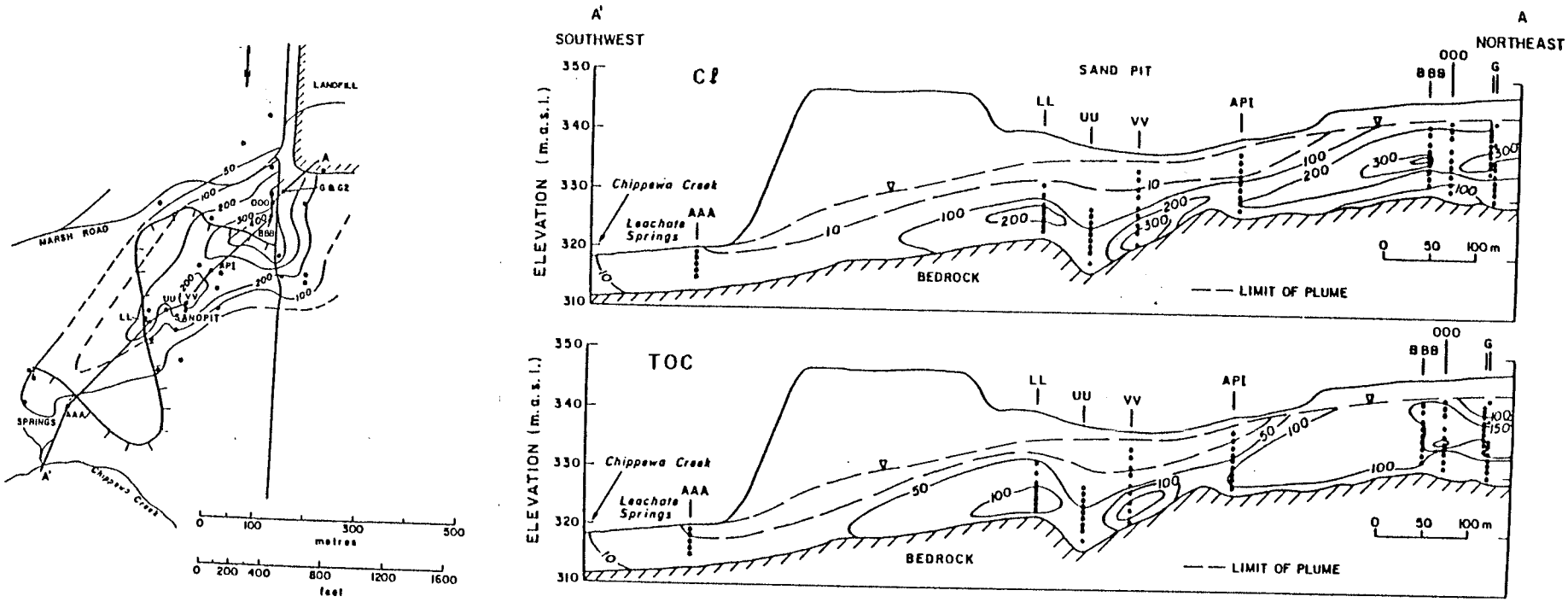

Figure 1. Plan view of the North Bay landfill leachate plume showing the distribution of maximum chloride (left) and the distribution of chloride (Cl) and total organic carbon (TOC) in groundwater along cross-section AA' (right). Concentration units are mg/L. (from Cherry et al., 1985)

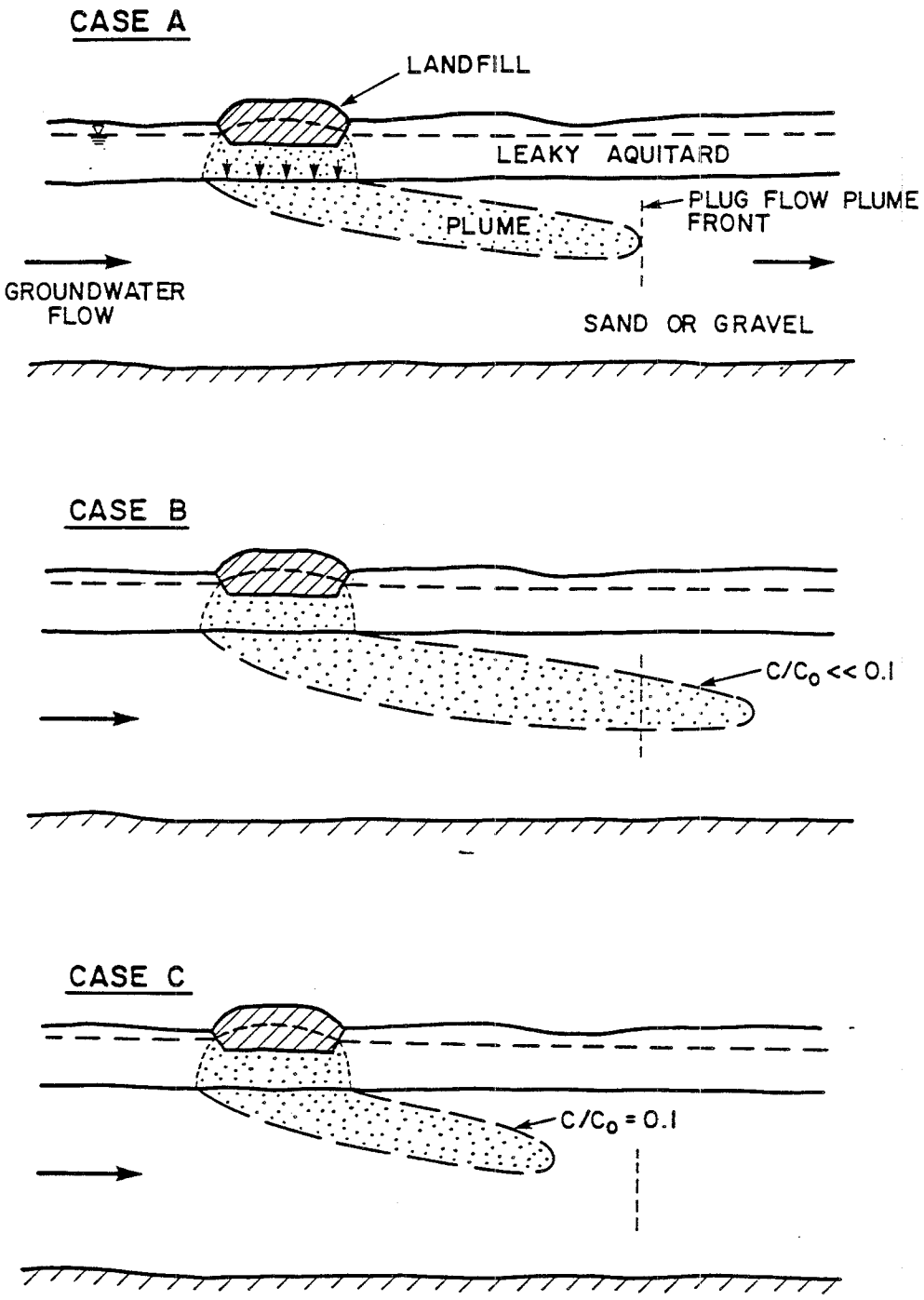

Figure 2. Conceptual examples of a landfill plume for conservative contaminants. Case A represents flow without dispersion; Case B and C represent flow with dispersion.

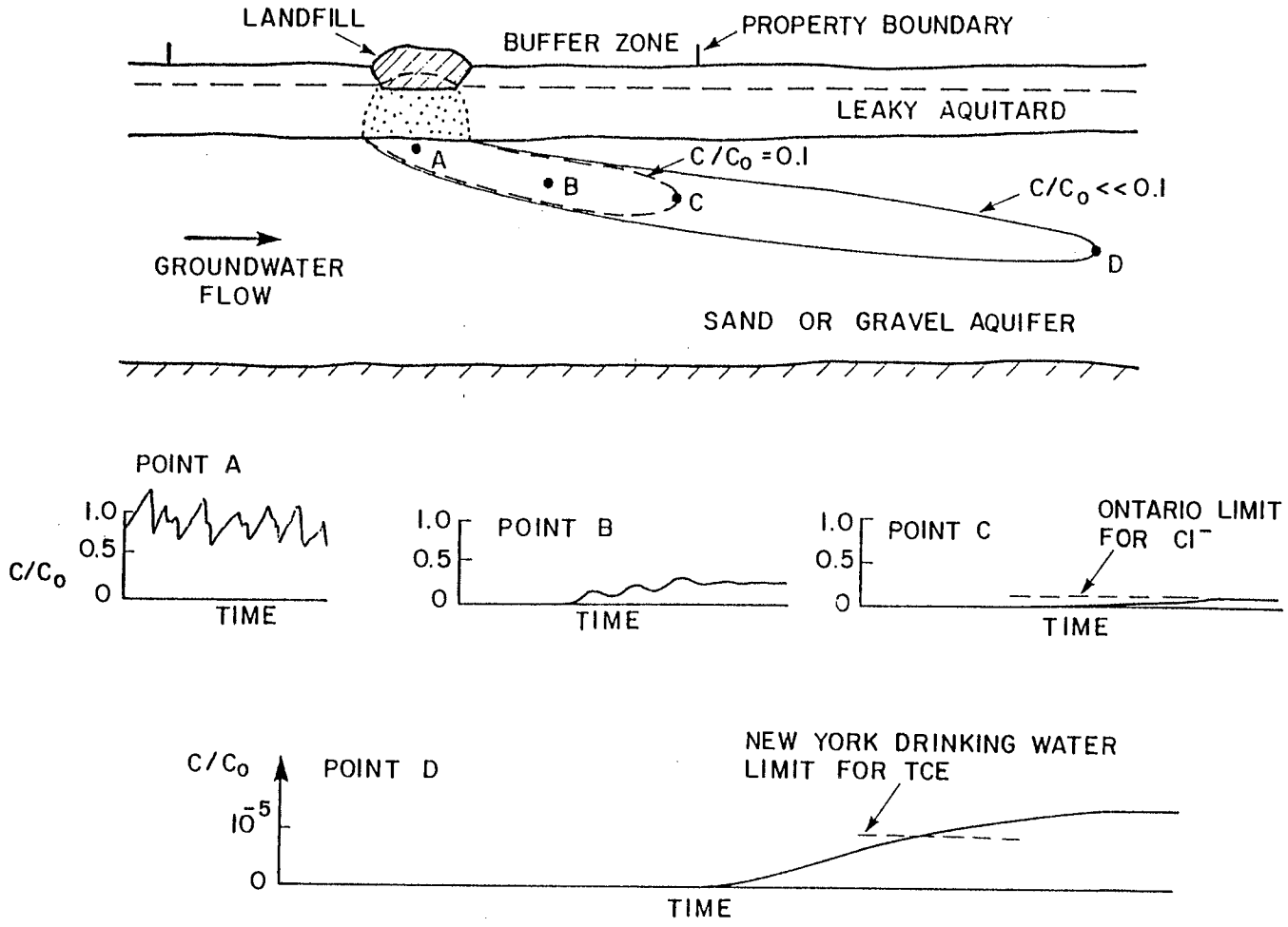

Figure 3. Achievement of steady-state relative concentrations at various points in a landfill leachate plume. (Co ≃ solubility of contaminant)

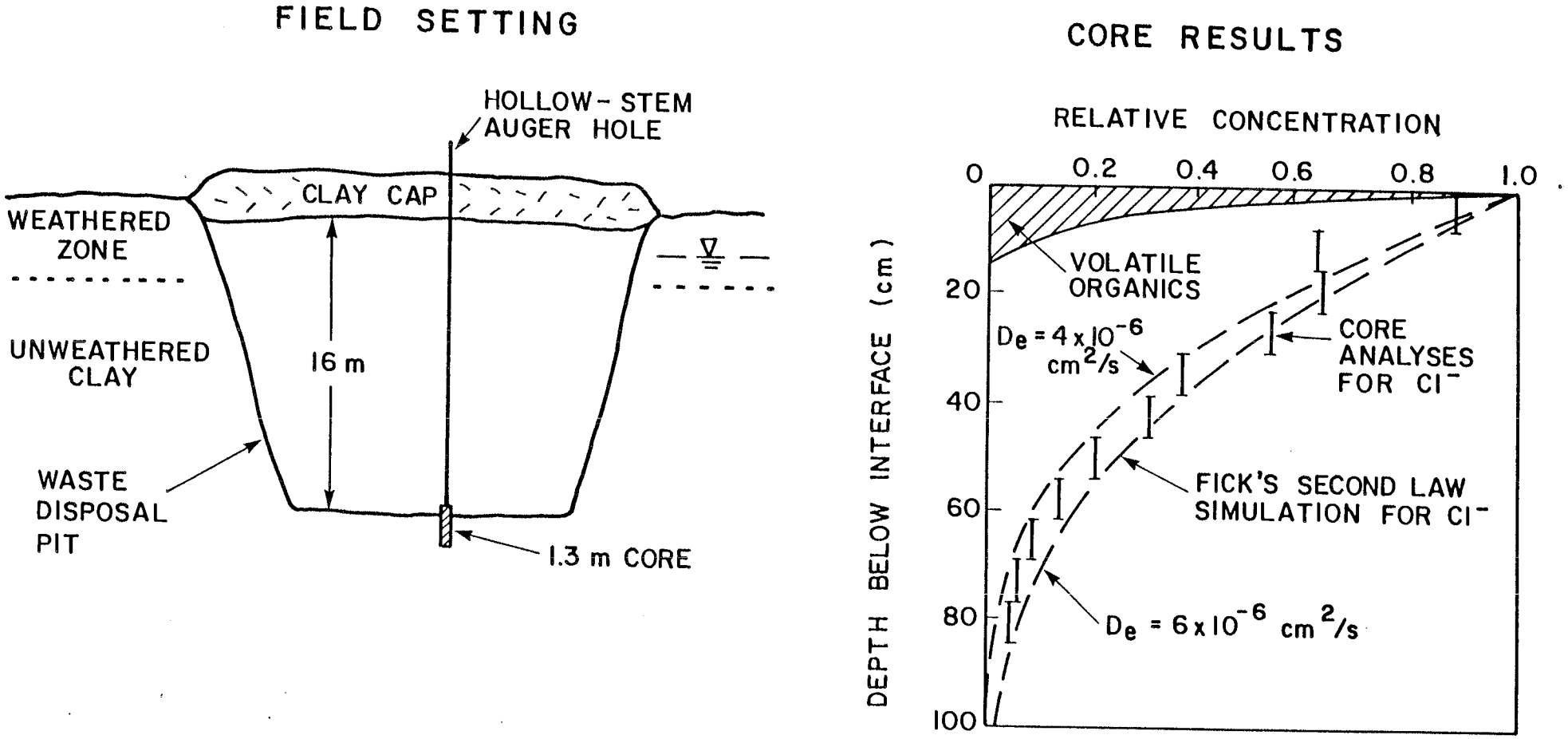

Figure 4. Waste disposal site field setting (left) and chloride (Cl) and organics distribution from core analysis (right). Dashed lines represent model predictions based on Fick's Second Law, where D_e is the effective diffusion coefficient.

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Faculty With Hydrogeological Research Interests

J.F. Barker, natural and industrial organic compounds in groundwater, biogeochemical transformations
J.A. Cherry, field studies of contaminant behavior, subsurface waste disposal
M.B. Dusseault, coupled flow-stress effects in porous media
R.N. Farvolden, evaluation of aquifer and aquitard systems, groundwater development
S.K. Frape, inorganic geochemistry of natural and contaminated groundwater
E.O. Frind, flow and transport processes, mathematical models
R.W. Gillham, soil physics, solute behavior in porous media, groundwater monitoring
J.P. Greenhouse, surface and borehole geophysics
E.J. Reardon, aqueous geochemistry, geochemical effects of infiltration, soil-gas transport
S. Schiff, isotopic and non-isotopic tracer of environmental processes, groundwater-surface water interactions.
E.A. Sudicky, dispersion, mathematical models

R.M. Brown, adjunct professor, Chalk River Nuclear Laboratory, AECL, environmental isotopes in groundwater studies
P. Fritz, environmental isotopes in studies of groundwater origin and age, Ins. fur Hydrologie, Fed. Rep. Germany
D.R. Lee, adjunct professor, Chalk River Nuclear Laboratory, AECL, biohydrology, groundwater-surface water interactions
G. van der Kamp, adjunct professor, Saskatchewan Research Council, aquifer analysis, groundwater recharge assessment.

Post-Doctorate Fellows and Research Associates

R.J. Drimmie, analytical techniques in isotope hydrology
C. Mase, pore-fluids and tectonic processes, contaminant transport in fractured media, mathematical modelling.
J. Hoff, Surface chemistry
K.-H. Spitz, Flow and transport modelling, aquifer decontamination.

Senior Technicians

S. O'Hannesin, groundwater laboratory
P.E. Johnson and R. Ingleton, development and testing of groundwater monitoring devices
R. Kellerman, Inorganic geochemistry laboratory
R. Dickhout, Organic geochemistry laboratory

April 12, 1988

Category Letter	Category Title
A	Flow and hydrogeochemistry of uncontaminated groundwater systems
B	Isotopic studies of the origin and age of groundwater
C	Movement of water, gas and solutes in the unsaturated zone
D	Surface water and groundwater/surface water interactions
E	Measurement and interpretation of contaminant transport parameters
F	Mathematical modeling of groundwater flow or contaminant transport in non-fractured systems
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P	Review papers and books
Q	Restoration/Reclamation of Contaminated Groundwater
R	Role of Groundwater in Geologic Processes

\+ Represents publications that are not available

A. FLOW AND HYDROGEOCHEMISTRY OF UNCONTAMINATED GROUNDWATER SYSTEMS

A-18 Frape, S.K. and Fritz, P., 1987. Geochemical trends for groundwaters from the Canadian Shield. In Saline water ans gases in crystalline rocks, Editors: Fritz P. and Frape, S.K.; Geological Association of Canada Special Paper 33, p. 19-38.

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